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DEVELOPMENT OF BUOY MOUNTED HYDROCARBON VAPOR SENSORS FOR USE I--ETC(U)
SEP 76 L H GOODSON, W B JACOBS, S DICK DOT-CG-34320-A

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PROJECT NO: 754241.2/13

DEVELOPMENT OF BUOY MOUNTED HYDROCARBON VAPOR SENSORS FOR USE IN LOCAL AREA POLLUTION SURVEILLANCE SYSTEMS

September 1976

FINAL REPORT

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16. Abstract

A low cost system for the rapid detection of small quantities of freshly spilled oil has been developed. This unit uses two Taguchi Gas Sensors (semiconductor, stannic oxide on a support), one of which responds to oil vapors and also to engine exhaust. The other sensor is protected by a semipermeable membrane (rubber dental dam) which has little or no effect on the response of the sensor to carbon monoxide yet is able to retard greatly the response to hydrocarbon vapors. The alarm logic is arranged so that an alarm is signalled when the uncovered sensor responds and the covered sensor does not. As a result, a high degree of specificity of the sensor system for oil spills has been achieved. Operation of the system for several months on the sea wall next to the ship channel in Galveston has shown a freedom from false alarms and good baseline stability. Additional studies with the system are recommended.

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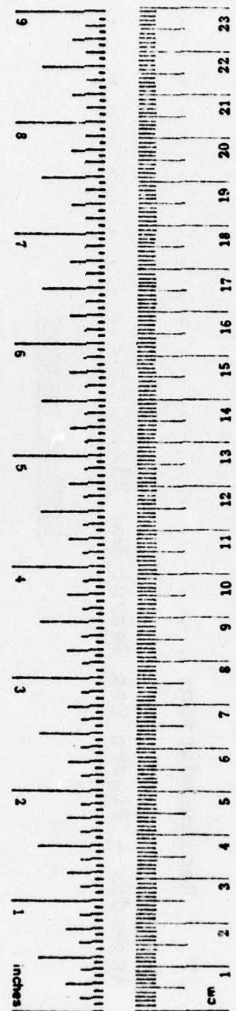
METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

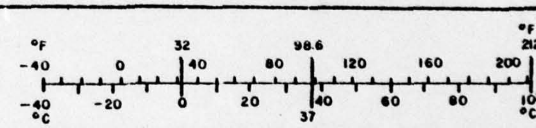
Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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I. INTRODUCTION

Previous reports on this contract (DOT-CG-34320-A, June 1975, INTERIM REPORT) described in-depth studies on the use of the Taguchi Gas Sensor (TGS) for the detection of petroleum vapors resulting from petroleum spills. The TGS sensor is a heated semiconductor chip which increases its conductivity when certain organic vapors are adsorbed on its surface. The principal active ingredient in the semiconductor chip is stannic oxide, which is heated with a resistance heater incorporated into the semiconductor chip. The heating serves to minimize the sensitivity of the system to water vapor and, at the same time, speeds the reversal of the adsorption process so that the sensor recovers quickly following its response to organic vapors.

The previous studies showed that fresh oil spills in a freshwater pond and also fresh spills in the Houston Ship Channel were readily detectable with the TGS sensor system. The quantity of oil detectable varied with the nature of oil spilled, the wind speed and other factors. However, in cases where crude petroleum was spilled on water in quantities as small as 25 ml and the sensor was located downwind from the spill, the sensors were able to provide signals well above the noise level in a few seconds. Responses to crude petroleum spills which had been stripped of their more volatile components (i.e., spills which had been aged for 24 hr) were often not detected by these TGS sensors.

A problem with these sensors which was considered troublesome was that they responded to exhaust from diesel and gasoline engines to giving signals which were indistinguishable from the signals obtained with the fresh oil spills.

The primary objectives of the current contract were:

1. Consider means of increasing the selectivity of the sensor system to oil vapors without interferring with the sensitivity of the TGS sensors.

2. Construct a buoy with TGS sensors which could be used in marine tests to demonstrate the stability of the system in all kinds of weather, its response to fresh spills, and at the same time demonstrate that the response of the sensor to exhaust vapors could be minimized or eliminated.

3. Conduct field studies with the optimized sensor system for a period of at least 6 months.

4. Provide drawings showing the electrical circuits used including specifically the alarm logic and remote signalling components.

The present report describes the TGS sensor system developed during this study and provides some test results which indicate typical results obtained during the field testing.

II. EXPERIMENTAL INVESTIGATIONS

A. Taguchi Gas Sensors (TGS)

For the present investigation only the Figaro Model No. 812 TGS sensors were used. These are general purpose transducers intended primarily for use on battery power and are operated with a heater voltage of 5 V ± 0.2 V and a sensor voltage of 10 V or greater (specifications do not list an upper voltage limit). Instead of the wire screen thimble cover, these sensors are mounted in a different style enclosure with screen wire discs located above and below the sensor (see Appendix); the vapor to be sensed passes in at the bottom and out the top with heat serving as the driving force. In the present No. 812 sensor, the heater circuit is not connected to the sensor circuit; this provides additional freedom in design of electronic circuits suitable for use with these sensors. Additional data on these sensors are provided in the Appendix.

Pretesting of the TGS 812 Sensors: Before putting new sensors into service they were tested to determine their warm-up curves, their response to standard hydrocarbon vapors, and the speed of their recoveries after removal of the hydrocarbon vapors. The results of these tests are shown in Table 1. Also shown in this table is the inspection data from Figaro showing the response of these same sensors to three different concentrations of isobutane. Sensor No. 63 had an unusual warm-up curve with maximum voltage ~50% of that seen for the other sensors. Its final equilibrated baseline voltage was unusually high and its response to hydrocarbon vapors was low; therefore, this one sensor was rejected from further study. The other sensors behaved very much alike and were considered to be satisfactory for the intended use.

B. Interference Studies

Limited studies have been conducted to determine which chemicals of commerce and which components of engine exhausts cause the TGS sensors to respond. It is well known that exhaust contains many incomplete combustion products including such things as saturated hydrocarbons, aromatic hydrocarbons, alcohols, ketones, acids, ethylenic and acetylenic compounds, oxides of nitrogen, and carbon monoxide. Various other chemicals of commerce have been added to this quantitative study of the sensitivity of the TGS sensors. Figure 1 provides the response of the TGS Model 812 sensors to 18 potential interfering substances. In the present study the sensors were placed in an 11.5-liter chamber with mechanical air circulation and the quantity of material required to produce a response of 0.5 V was measured. From the data on the graph it may be noted that ligroine responded at 7 ppm and that of the other materials only benzene and ethylene dichloride

TABLE 1. INSPECTION OF NEW TGS SENSORS

Sensor No.	Typical Warm-Up Curve[a/]	Baseline in Air Volts	Response to Air Saturated With No. 2 Fuel Oil Vapor, V[b/]	Recovery Time, Min	Figaro Inspection Data[c/] R_1/R_2	Figaro Inspection Data[c/] R_2, Kohms	Figaro Inspection Data[c/] R_3/R_2
61	yes	0.40	8.30	6	1.4	3.4	0.60
62	yes	0.30	7.75	4	1.4	3.2	0.59
63[d/]	no	1.60	1.95	2.5	1.4	3.8	0.61
64	yes	0.30	8.85	6	1.4	2.7	0.63
65	yes	0.25	8.25	5	1.4	3.0	0.62
66	yes	0.20	8.55	8	1.4	3.3	0.64
67	yes	0.20	7.05	5	1.5	6.0	0.59
68	yes	0.20	8.30	8	1.4	3.8	0.61
69	yes	0.20	8.15	6	1.4	3.2	0.60
70	yes	0.25	9.05	10	1.4	2.6	0.61
71	yes	0.30	8.90	9	1.4	3.1	0.60
72	yes	0.40	9.45	9	1.4	2.4	0.63
73	yes	0.25	8.40	6	1.4	3.5	0.62
74	yes	0.20	7.60	5	1.4	4.2	0.64
75	yes	0.25	8.15	6	1.4	3.4	0.60
76	yes	0.30	7.95	6	1.4	3.1	0.58
77	yes	0.50	9.30	6	1.4	2.2	0.62
78	yes	0.45	8.55	5	1.4	2.6	0.62
79	yes	0.40	7.75	4	1.4	3.6	0.63
80	yes	0.35	8.05	5	1.4	3.1	0.57

a/ In the typical warm-up the voltage rises immediately 8-12 V and then falls to 1.0 V in ~2 min and reaches a stable baseline value in 5-10 min.

b/ Test bottle contained 1 ml of No. 2 fuel oil, 20 ml of water and 500 ml of air.

c/ R_1, R_2, and R_3 are the resistances of the sensors in the presence of isobutane in air at the concentrations of 500, 1,000 and 3,000 ppm, respectively.

d/ This sensor was rejected because of high baseline and low response to fuel oil vapors.

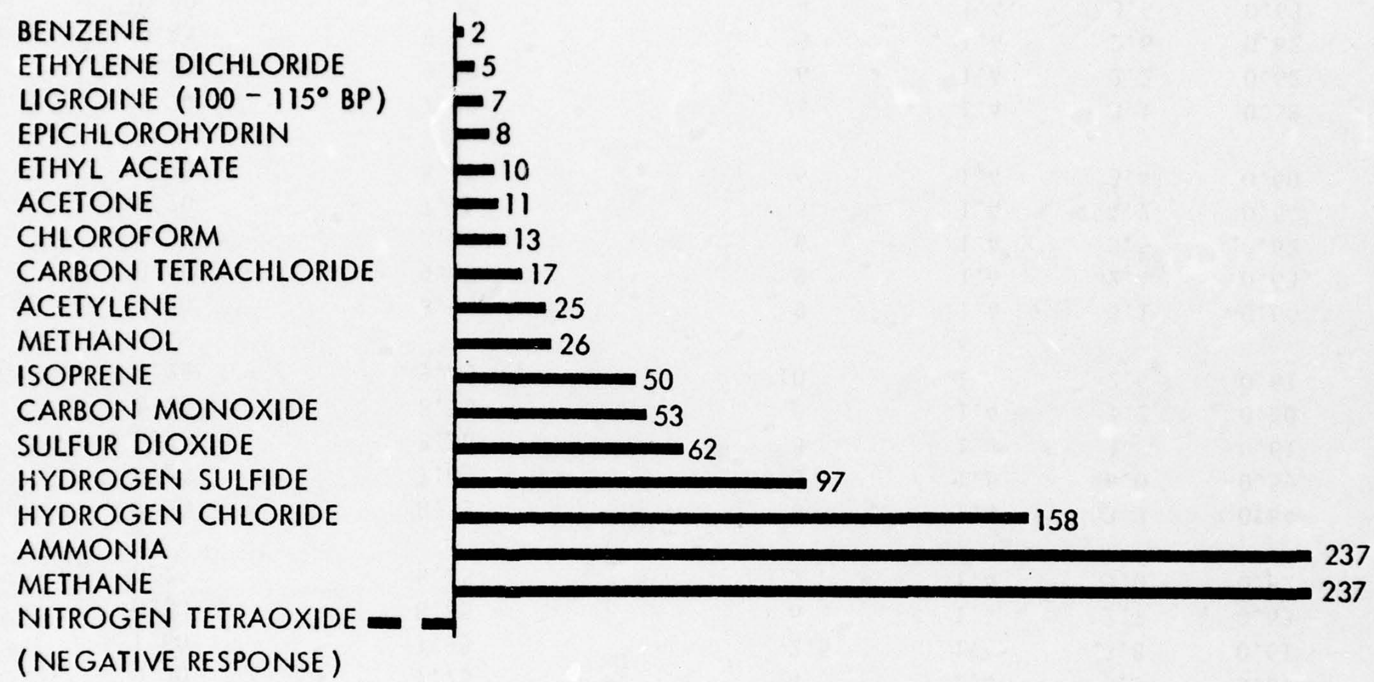


Figure 1 - Concentrations of Hazardous Vapors (ppm) Producing a Response of 0.5 V

were detectable at lower concentrations. Since the volatiles in crude petroleum consist mainly of the low boiling straight chain aliphatic hydrocarbons (closely related to ligroine which is of petroleum origin), it is clear that the TGS sensor is well suited for use in the measurement of fresh petroleum spills.

It was surprising that no concentration of nitrogen dioxide gave a positive response and that responses to methane and ammonia were obtained only at levels 30 times higher than the level at which ligroine was detected.

The moderately high response of the TGS sensors to carbon monoxide probably explains why automobile exhaust caused the high responses seen in the earlier studies with the TGS sensor system in the marine environment when boats or larger craft passed near the sensors (see previous report on this contract). Internal combustion engines are notoriously large CO generators and exhaust containing more than 10,000 ppm would probably not be unusual.

In view of the possibility that CO was the material in engine exhaust causing the response of the TGS sensors, some limited studies were done in which automobile exhaust was collected in a 50-gal. plastic bag and then extracted with a CO absorbent (i.e., cuprous chloride and hydrogen chloride). After contacting the exhaust with the CO absorbent, the exhaust was passed through a KOH trap to remove the HCl. When this gas was admitted to the sensor chamber it was evident that this treatment had significantly reduced the sensor response. This result was interpreted to mean that CO caused a significant part, if not all, of the interference experienced with the exhaust. Further study will be required to determine if other compounds in exhaust also cause interference problems.

C. Modification of Sensor Specificity

A potential method for improving the selectivity of the TGS sensors for oil vapors is described here. The basic idea behind these experiments was that a TGS sensor could be made specific for carbon monoxide vapor by covering it with a membrane which was permeable to carbon monoxide and impermeable (or only slowly permeable) to hydrocarbon vapors. Thus, through the simultaneous use of two sensors, one of which responds only to CO and the other of which responds to both CO and hydrocarbons, it should be possible to subtract electrically the response of the CO sensor from the CO-hydrocarbon sensor. This process should then give improved selectivity of the TGS sensors for hydrocarbon spills. This expected result was based upon the assumption that the principal substance in gasoline engine exhaust causing the TGS response was carbon monoxide.

For the present study, four TGS sensors (Type 812) were placed in a 11.5-liter test chamber with mechanical air circulation and exposed to a series of test vapors at known concentrations. In this study the first sensor was uncovered, the second was covered with a sheet of rubber dental dam, the third was covered with Saran® Wrap and the fourth was covered with cellulose dialysis tubing. In each case the covers were applied to the outside of 4-in. long wind screen wire cylinders which were used to cover all the sensors. The responses of these membrane covered and uncovered sensors to the different vapors are shown in Table 2. The rubber dental dam was effective in slowing the response of the sensor to both ligroine and also to Skellysolve® B vapors without reducing the response to carbon monoxide. Additional testing of the sensors with the rubber dental dam covers is presented in Figure 2 and 3. With the uncovered sensor (Figure 2) it was shown that there was good response to Skellysolve B in the absence of CO; in the presence of 183 ppm CO there was little effect on adding the Skellysolve B. Thus, this uncovered sensor reacts well to both Skellysolve B and also to CO.

Figure 3 presents the response of the TGS sensor covered with rubber dental dam. In this case the response of the sensor to Skellysolve B is much retarded while the response to carbon monoxide is about the same as that shown for the uncovered sensor (shown in Figure 2).

In an effort to replace the rubber dental dam with a material which had superior weathering characteristics and/or improved ability to shield the TGS sensor from oil vapors, replacement of the rubber dental dam with a (1) silicone rubber sheet (7 to 9 mil) was investigated. Unfortunately, the hydrocarbon vapors permeated the silicone rubber quickly and it was judged unsuited for the making of a CO sensor. Two other membranes were examined and these were (2) a water dispersed rubber latex applied to the brass windscreen cover and (3) a toluene dispersed white rubber latex applied to the brass wind-screen cylinder enclosing the sensor. These membranes were also rejected because they did not appreciably slow the response of the sensors to hydrocarbon vapors.

D. Buoy System Circuitry and Alarm Logic

While the buoy system was in the field a variety of electronic circuits, sensor arrangements and alarm logics for two sensors were investigated for the purpose of minimizing the power requirements, obtaining stability of operation and obtaining a high degree of selectivity for the oil vapors.

In one set of experiments the filaments of a membrane covered and an uncovered TGS sensor were connected together as a means to improve the power efficiency when operating two 5-V sensor heaters from a 12-V battery.

TABLE 2. RELATIVE SENSITIVITY OF COVERED AND UNCOVERED TGS SENSORS TO KNOWN VAPORS[a/]

Test Vapor	Vapor Conc., ppm	No Membrane	Rubber Dental Dam	Saran® Wrap	Cellophane Dialysis Tube
Gasoline Engine Exhaust (w/choke)	70,000	4.95	6.35	6.30	5.30
Gasoline Engine Exhaust (w/out choke)	70,000	6.20	7.95	7.90	7.60
Carbon Monoxide	450	1.60	2.55	1.85	2.05
Carbon Monoxide	367	1.60	2.00	1.50	1.30
Carbon Monoxide	100	0.51	0.95	0.60	0.55
Carbon Monoxide	63	0.60	0.55	0.45	0.35
Ligroine (BP = 100°-115°)	100	1.55	0.45	0.80	0.85
Skellysolve B	100	2.00	1.10	1.40	1.10
NO_2[b/]	870	-0.30	-0.50	-0.70	-0.90
Acetylene	40	0.80	0.50	0.30	0.30
Acetylene	87	2.50	3.50	3.15	2.55

a/ Tests carried out in 11.5 liter chamber using TGS No. 812 sensors; responses are given in volts change from baseline.

b/ Impure nitrogen tetraoxide generated by the reaction: $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + \underset{\text{(red/brown)}}{2NO_2 \uparrow} + 2H_2O$.

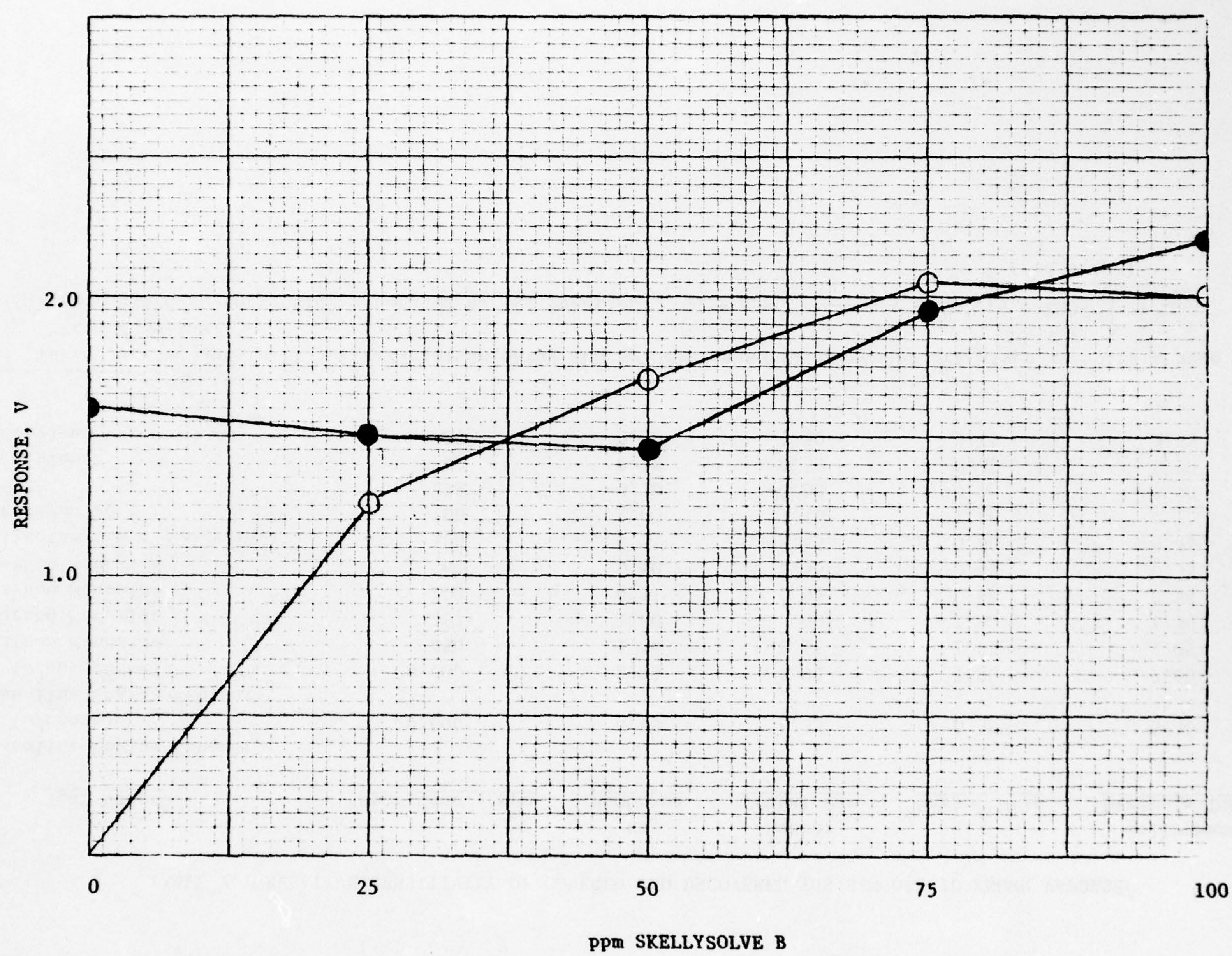


Figure 2. Response of TGS Uncovered Sensor to Skellysolve B (○) or to Skellysolve B + 183 ppm CO (●).

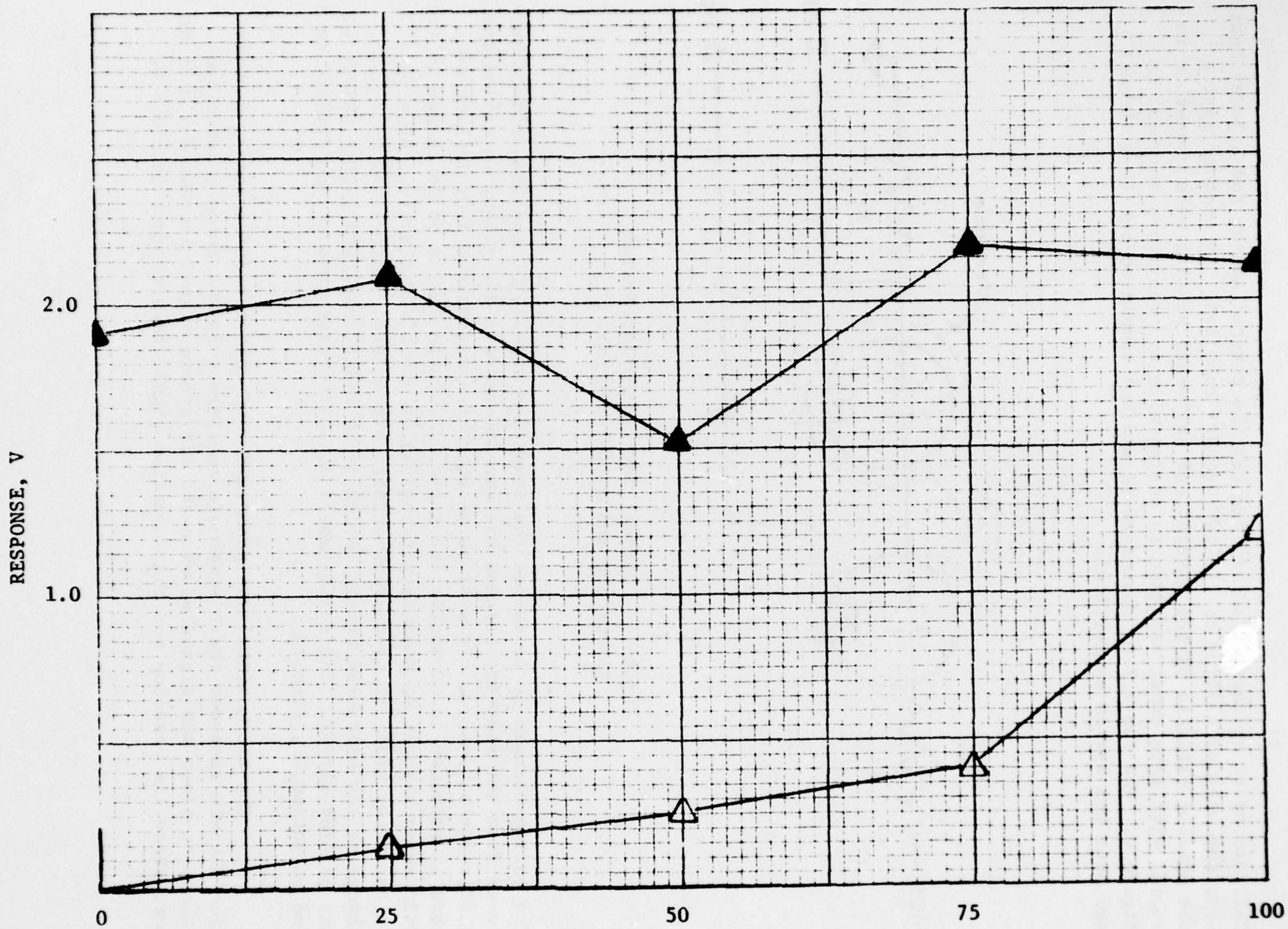


Figure 3. Response of TGS Sensor Covered with Rubber Dental Dam to Skellysolve B (△) or to Skellysolve B + 183 ppm of CO (▲).

This proved to be unsatisfactory because the covered sensor had a lower heat loss and unequal heating of the two sensors resulted. In another approach the sensing circuits of the covered and uncovered sensors were connected in series with each other and also in series with two resistors as shown in Figure 4. The two 4.7 KΩ resistors (R and R_L) completed the 10-V circuit and made the system symmetrical.

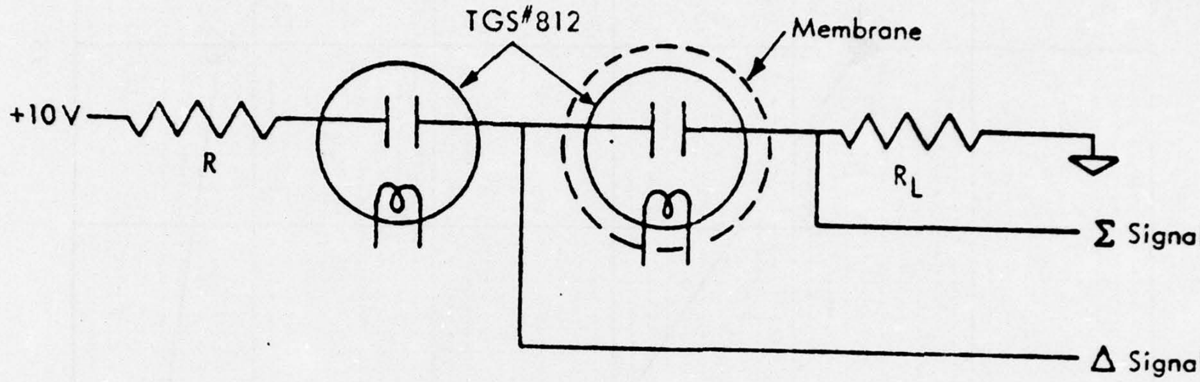


Figure 4 - Circuit for Two Sensor System
(Summation and Difference Circuit)

The voltage across R_L is called the summation signal, Σ, and the voltage measured from the midpoint between the two TGS sensors and ground is called the difference signal, Δ. It will be noted that a resistance drop in both sensors in response to CO would, theoretically, cause little or no change in the difference signal, Δ, because both halves of the circuit would change equally. On the other hand, if hydrocarbon vapors are sensed, there would be a big change in the uncovered sensor (decrease in resistance) and little change in the covered sensor. The result would be an increase in both the difference Δ and summation, Σ, signals.

The alarm signal was generated when both the difference and summation signals exceeded their threshold settings. In the example described below, an alarm was signalled when the difference signal increased a volt or more above its baseline and the summation signal rose to more than 0.8 V.

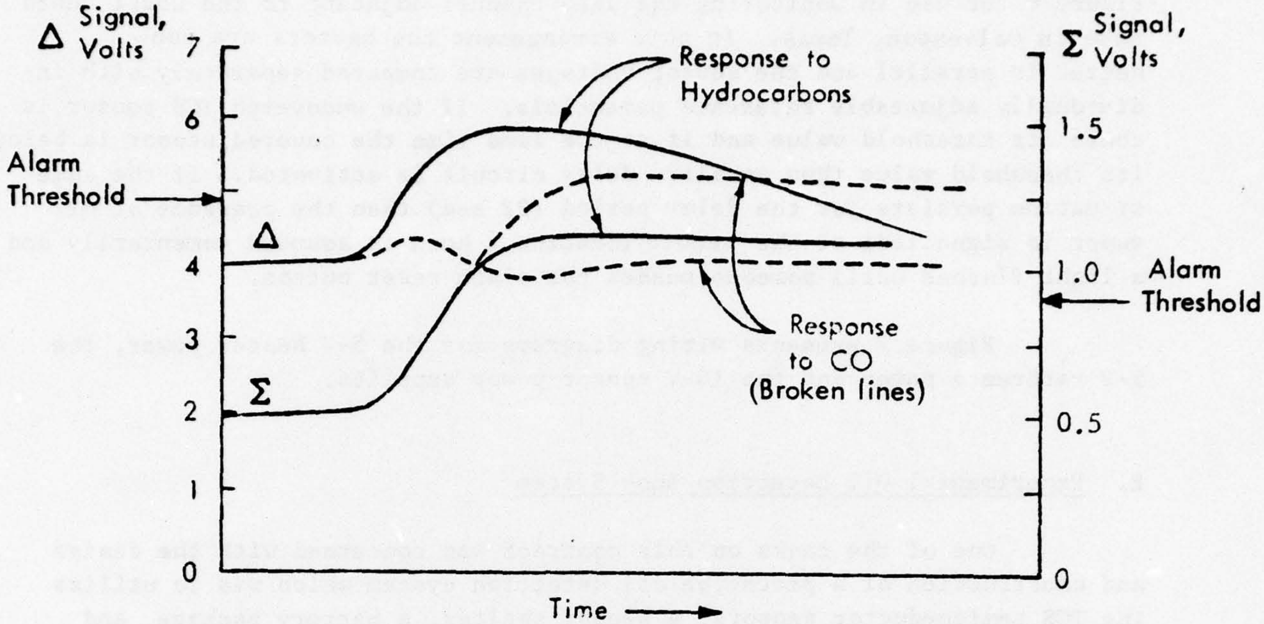


Figure 5 - Predicted Response of the Two Sensor Circuit to CO and Hydrocarbon Vapors

As may be seen from the curve (Figure 5) the difference and summation signals ($\Delta + \Sigma$) would have given an alarm to hydrocarbon vapors and no alarm from CO. Although the present logic required both the difference and summation signals to exceed their threshold settings, no time delay was needed. This was the circuit used in the buoy system at the MRI lake.

The big problem with these two variations of the same sensor system was that: (1) Both exhaust and oil vapors produced large responses; (2) recovery of the initial baseline voltage following exposure was very slow, sometimes requiring as much as an hour; (3) there was much noise in the baseline voltage between exposures; and (4) it was difficult to determine how each sensor was responding.

In an effort to minimize false alarms with the two sensor system for oil spill detection, it was decided that a time delay would be useful. It was reasoned that a boat or ship passing by the buoy might result in the momentary exposure of the sensor to exhaust but that a spill should persist for at least 22 sec if it were large enough to be of interest. The delay circuits were arranged so that the alarm logic would need to be satisfied for 22 sec continuously before an alarm signal would be sounded.

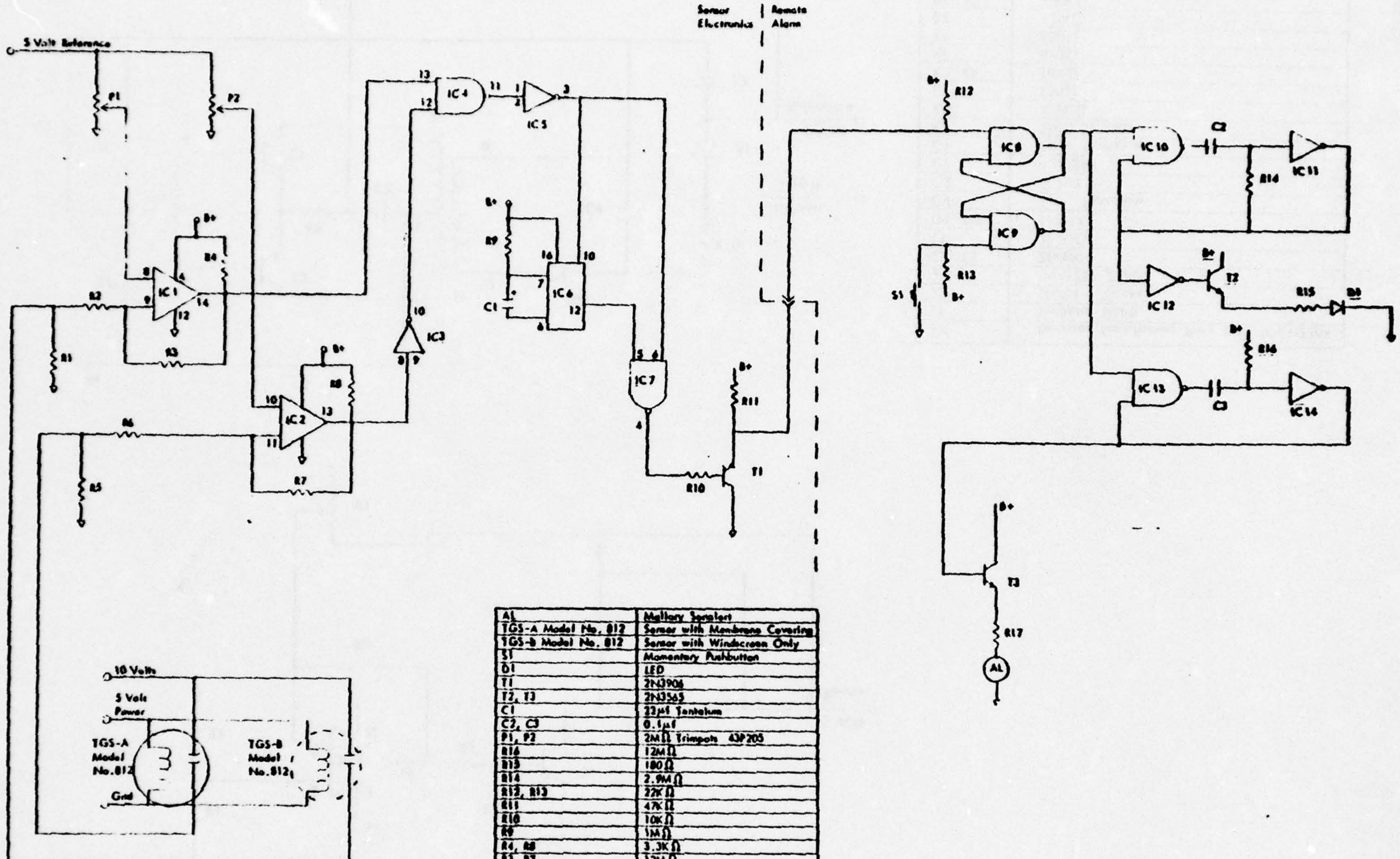
As a result of these experiments we selected the circuit shown in Figure 6 for use in monitoring the ship channel adjacent to the Coast Guard Base in Galveston, Texas. In this arrangement the heaters are connected in parallel and the sensor voltages are compared separately with individually adjustable reference potentials. If the uncovered TGS sensor is above its threshold value and if at the same time the covered sensor is below its threshold value then an alarm delay circuit is activated. If the same situation persists for the delay period (22 sec) then the presence of oil vapor is signalled; at the remote location a horn is sounded momentarily and a light flashes until someone pushes the alarm reset button.

Figure 7 presents wiring diagrams for the 5-V heater power, the 5-V reference power and the 10-V sensor power supplies.

E. Experimental Oil Detection Buoy System

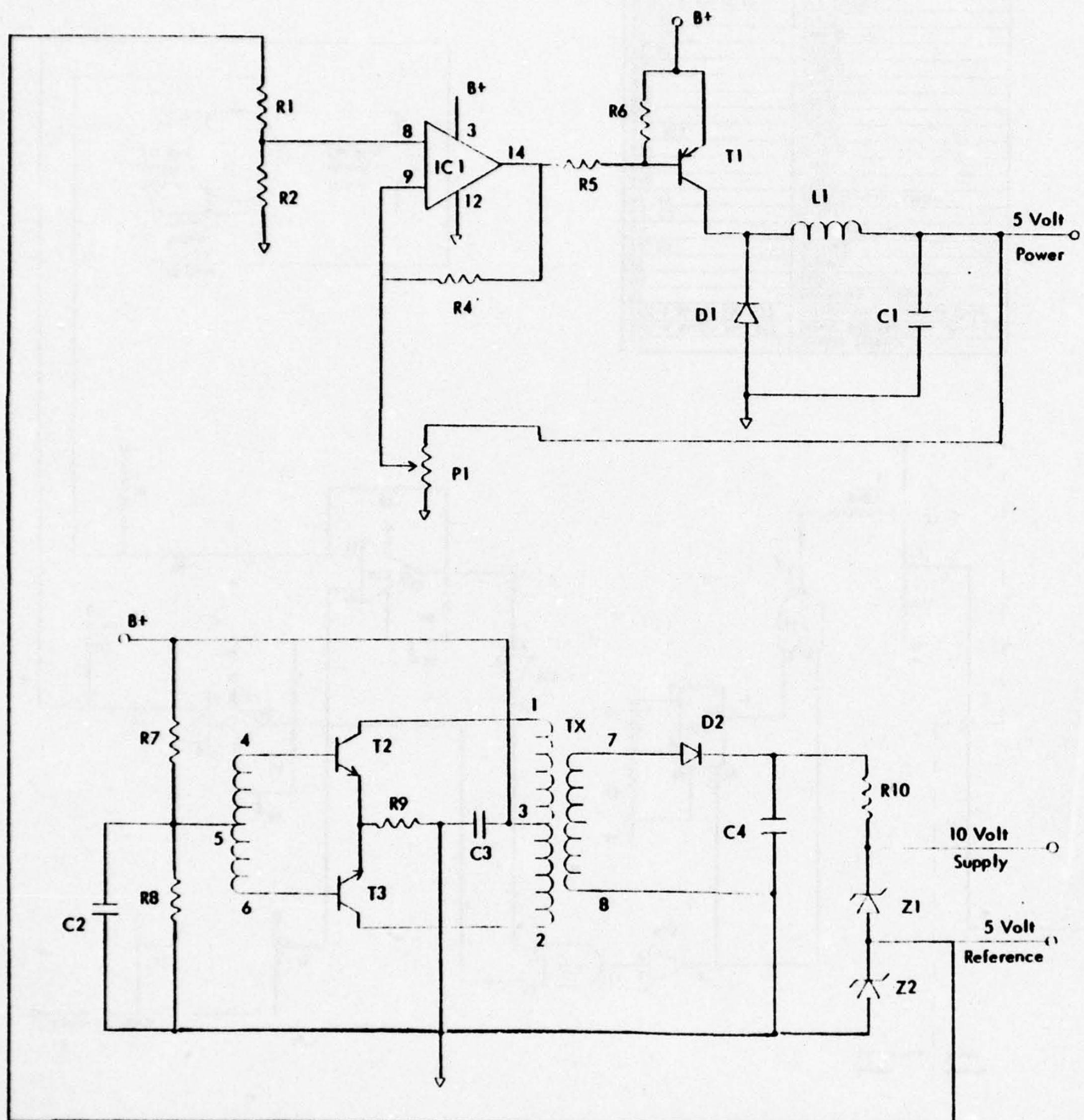
One of the tasks on this contract was concerned with the design and construction of a prototype oil detection system which was to utilize the TGS semiconductor sensors, a sensor shelter, a battery package, and electronics package with suitable alarm logic. It was intended that this system would be mounted close to shore and, therefore, could use hard wire rather than telemetry to signal the presence of fresh oil spills.

1. The Sensor Shelter: Previous studies with sensors in a marine environment showed that (1) the sensors must not get wet (wet sensors respond like sensors exposed to oil vapors), (2) the sensors must be protected from wind gusts so that noisy baseline voltages can be avoided, and (3) the sensors must be readily accessible to the vapors from oil spills. Studies with chimneys as covers for sensors showed that they require forced ventilation for reliable performance; that is, the chimneys cause either up-drafts or down-drafts depending upon the weather, sunlight, etc. Since power for forced ventilation in the chimneys is not available on the buoys, alternative sensor enclosures were sought. For some studies the TGS sensors were mounted at the upper end of a piece of plastic pipe, 1 in. ID and 4 in. long; tests showed that the vapors did not get to the sensors fast enough. The preliminary sensor shelter design is shown in Figure 8. The shelter was made from sheet aluminum; the openings in the walls on four sides are covered on the inside with both screen wire and louvers which are arranged so that there will be no straight-line path from outside the shelter to the sensors which are mounted on the upper inside. As shown in the Figure 8 insert, one of the cylindrical wind-screen covers has been removed to show the location of the sensors on a cross-member in the upper part of the shelter. A door provides access to the sensors for making standard exposures to hydrocarbons and also for servicing.



AL	Mallory Sonalert
TGS-A Model No. 812	Sensor with Membrane Covering
TGS-B Model No. 812	Sensor with Windscreen Only
S1	Momentary Pushbutton
D1	LED
T1	2N3906
T2, T3	2N3565
C1	22µf Tantalum
C2, C3	0.1µf
P1, P2	2MΩ Trimpots 43P205
R16	12MΩ
R15	180Ω
R14	2.9MΩ
R12, R13	22KΩ
R11	47KΩ
R10	10KΩ
R9	1MΩ
R4, R8	3.3KΩ
R3, R7	12MΩ
R2, R6	680KΩ
R1, R5	10KΩ
IC 12, IC 13, IC 14	1/4 CD4001
IC 8, IC 9, IC 10, IC 11	1/4 CD4011
IC 6	1/2 74C221
IC 3, IC 4, IC 5, IC 7	1/4 CD4011
IC 1, IC 2	1/4-74C909 or 1/4 LM324

Figure 6. Schematics for the TGS Oil Vapor Sensing System Including Both Sensor Electronics and Remote Alarm (see Figure 7 for Power Supply)



TX	Inverter Transformer Poly Paks 92CU2364
L1	Inductor 80μh
Z2	IN751 Zener
Z1	IN4575 Zener
T2, T3	2N3904
T1	2N3120
D1, D2	IN914
C4	1μf Tantalum
C3	0.1μf
C2	0.005μf
C1	1μf Tantalum
P1	1MΩ Trimpot
R10	4.7KΩ
R9	150Ω
R7, R8	10KΩ
R6	820Ω
R5	680Ω
R4	12MΩ
R1, R2	470KΩ
IC1	1/4-74C909 or 1/4 LM324

Figure 7. Power Supplies for the TGS Oil Sensing System

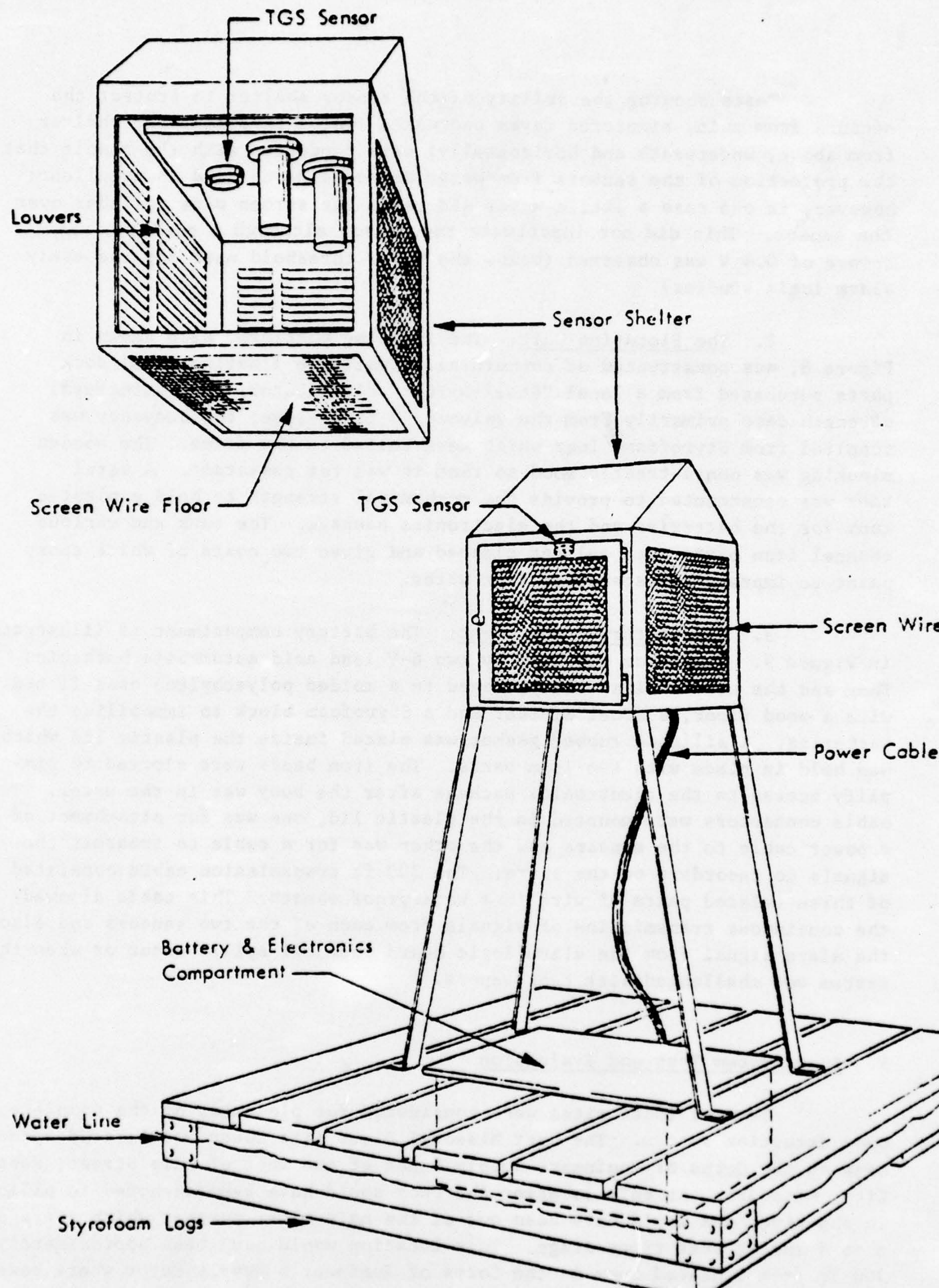


Figure 8. Pollution Surveillance Buoy Showing Flotation Platform, Sensor Shelter and Battery Compartment.

Tests showing the ability of the sensor shelter to protect the sensors from rain, simulated waves and wakes (water thrown at the shelter from above, underneath and horizontally) were conducted with the result that the protection of the sensors from water was considered good to excellent; however, in one case a little water did reach the screen wire cylinder over the sensor. This did not inactivate the sensor although a positive response of 0.4 V was observed (below the 0.5-V threshold used for the early alarm logic studies).

2. The Flotation Unit: The floating platform, also shown in Figure 8, was constructed of commercially available floating steel dock parts purchased from a local "Steel-N-Foam" distributor. The structural strength came primarily from the galvanized iron frame; the buoyancy was supplied from Styrofoam® logs which were bolted to the frame. The wooden planking was penta-treated wood so that it was rot resistant. A metal tank was constructed to provide the mechanical strength to hold a plastic tank for the batteries and the electronics package. The tank and various channel iron parts were solvent cleaned and given two coats of white epoxy paint to improve resistance to salt water.

3. The Battery Compartment: The battery compartment is illustrated in Figure 9. Power was supplied by two 6-V lead acid automobile batteries. They and the electronics were packaged in a molded polyethylene case fitted with a wood floor, a steel divider and a Styrofoam block to immobilize the batteries. A silicone rubber gasket was placed inside the plastic lid which was held in place with two iron bands. The iron bands were slotted to simplify access to the electronics package after the buoy was in the water. Two cable connectors were mounted in the plastic lid, one was for attachment of a power cable to the sensors and the other was for a cable to transmit the signals to recorders on the shore. The 300-ft transmission cable consisted of three twisted pairs of wire in a waterproof sheath. This cable allowed the continuous transmission of signals from each of the two sensors and also the alarm signal from the alarm logic board when oil spills occur or when the system was challenged with test vapors.

F. Buoy System Test and Evaluation

Several local sites were considered for placement of the completed buoy detection system. The best Missouri River site found was located adjacent to the Corps of Engineers Supply Depot at the foot of Main Street, Kansas City, Missouri. At this location the buoy could have been anchored to piling in the river and would have been out of the main river current which averaged 6 to 8 mph at that river stage. This location would have been approximately 300 ft from a heated room in the Corps of Engineer's Supply Depot where power would have been available and where the recorders to monitor the alarm logic

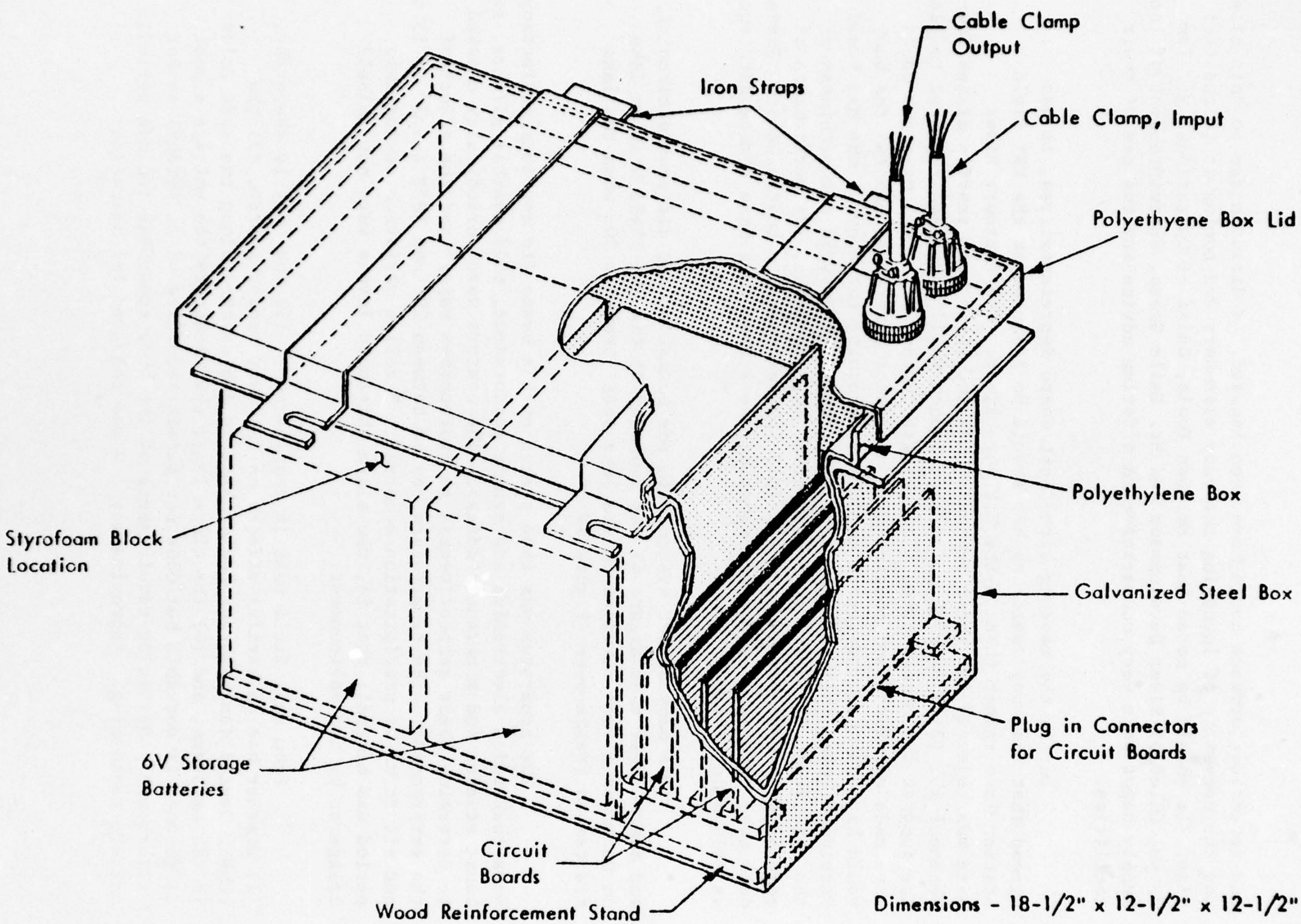


Figure 9. Batteries and Electronics Cases

and sensor performance could have been located. A disadvantage to this site was the necessity of launching the buoy elsewhere and towing it to the test site. It should be noted that Mr. Don Poole, Chief of Operations, Mr. Tom Burke, Chief of River Development and Mr. Emile Gross, Superintendent of the Supply Depot were very cooperative in offering advice and the use of their facilities.

During the meeting with Coast Guard Representatives, it was agreed that the buoy sensor system should be launched at the MRI Field Station lake rather than in the Missouri River. The Missouri River site was rejected for these reasons: (1) the river boat traffic closes down December 10, (2) a derrick or a river launch would have been required to place the buoy at the chosen site, (3) the fast current of 6 to 8 miles/hr would have made servicing and routine test exposures hazardous, and (4) the buoy would have been attractive to vandals. Launching the buoy at the MRI Field Station allowed collection of data concerning (1) overall seaworthiness of the apparatus, (2) development of servicing procedures, (3) performance of components, (4) power consumption and, (5) responses to boat exhaust. These data were necessary before transporting the system to a more remote site such as Galveston, Texas.

The buoy sensor system with the summation and difference circuitry and alarm logic (see Figure 4) was launched at the MRI Field Station lake on December 1, and remained in the lake until December 30, when the lake started to freeze over (Figure 10).

The apparatus was then placed on the beach (to continue collecting data concerning electronics and sensor performance, cold weather effects, exhaust studies and membrane studies). The sensors were periodically checked to determine their responsiveness to hydrocarbon vapors and the effect of the environment. The temperature varied between 20° and 60°F (-6.7° to 15.6°C) and all forms of precipitation occurred. Baseline variation during this period was minimal; that is, the alarm threshold levels were not falsely triggered by the environment.

From this field test it was learned: (1) the buoy is seaworthy, (2) weather has no harmful effects on the buoy sensor system, (3) the rubber dental dam membrane became brittle and cracked along the soft folds in the membrane, and (4) the alarm logic that monitors the voltage signal difference is workable but does not permit recording of individual sensor performance. Servicing requirements of the buoy apparatus include periodic battery recharging. Approximately 1 W was required for operation.

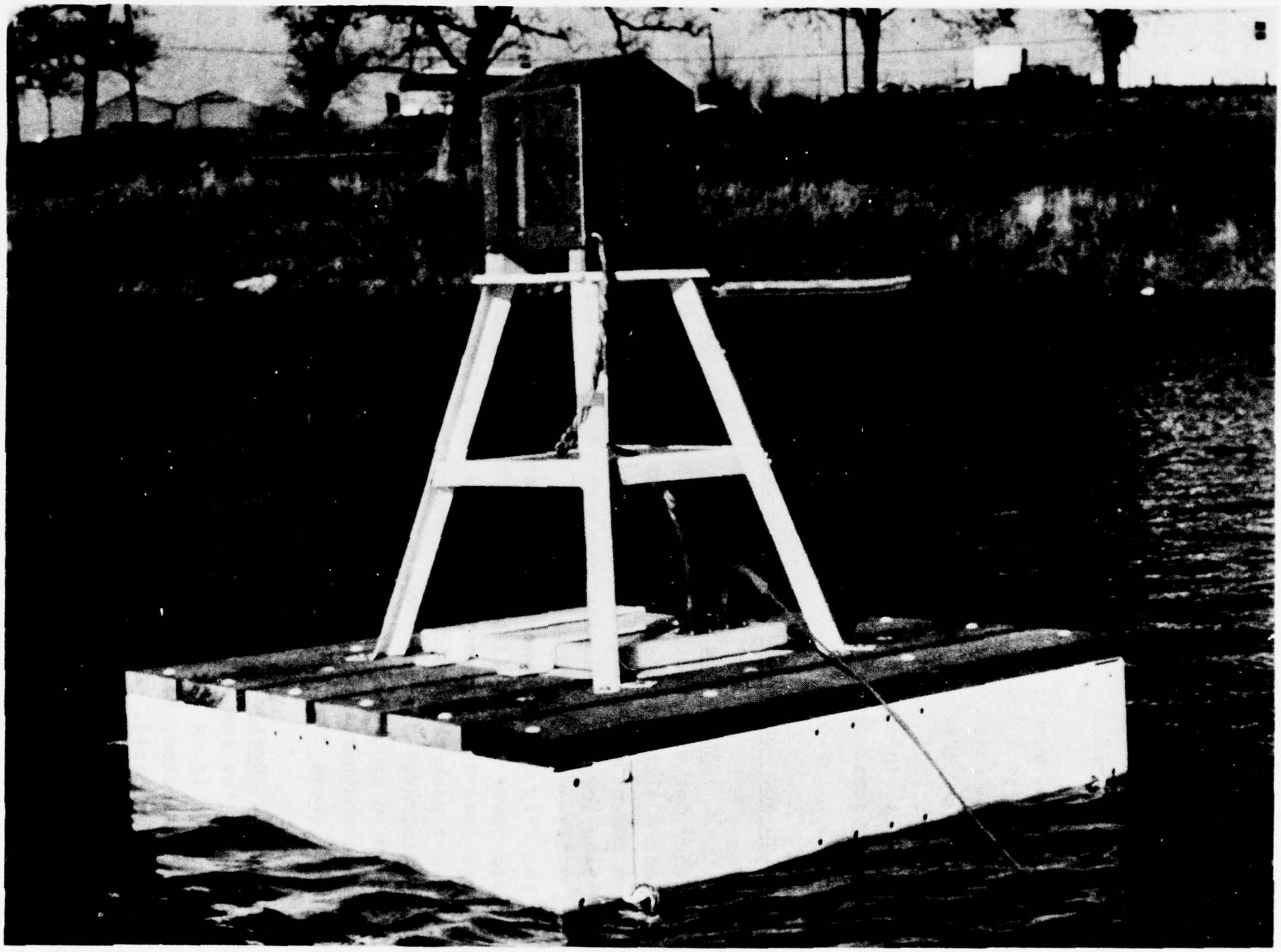


Figure 10. Buoy Sensor System Operating on Battery Power in MRI Lake.

The batteries operated two sensors and the alarm logic for 550 hr before failing to power the sensors. The batteries used had a rated capacity of 134 amp-hr at 12 V, much less than the Coast Guard buoy batteries for which the sensors were designed. Routine servicing also included frequent visual inspections and standard exposure to hydrocarbon vapors from which reliability data was gathered.

As a result of these buoy sensor system studies several changes were suggested: (1) a low-battery signal should be sent to the recorders on shore; this would indicate when recharging was needed; (2) cleats should be mounted to the deck of the buoy so that the buoy can be lashed to a boat or a pier during servicing; (3) a new membrane holder design was needed which to eliminate the folds in the rubber dental dam, and (4) circuit modifications was needed to permit observation of individual sensor performance.

G. Design and Construct Prototype Oil Detection Buoy System

1. Site Selection: On January 21, Mr. William Jacobs of our laboratory met with Lt. George White of the U.S. Coast Guard in Galveston to select a site for the further evaluation of the TGS sensor system. A site on top of a sea wall within 400 ft of the Coast Guard Base in Galveston was chosen for the following reasons: (1) this site placed the sensor between 2-1/2 and 5 ft above the water (depending on the tide) and about 20 ft from the ship channel where Coast Guard vessels and oil tankers pass; (2) electric power was available so that it was not necessary to transport or recharge lead-acid batteries for this test; (3) is was possible to hard wire the sensor package to recorders under the ramp at the Coast Guard Building which eliminated the need for telemetry; and (4) an alarm signal could be placed in an area where personnel were available to respond to alarms and to determine whether the TGS sensor response was due to oil or to interferences. Figure 11 shows two views of the selected site.

2. Design Changes: Because the sensor enclosure would be mounted directly on the sea wall, basic design changes were required. A small steel enclosure (6 in. x 5 in. x 4 in.), open only at the bottom and without louvers was selected, see Figure 12. The design of the cylindrical wind-screen covers was altered. A small square of stainless steel screen was rolled and soldered to a solid brass cap on one end and a brass cylinder on the other end. The cylinder was attached to the Plexiglas® support and it enclosed the sensor. This design was chosen because a sheet of rubber dental dam could be easily and smoothly attached to the screen and this would extend the lifetime of the membrane.

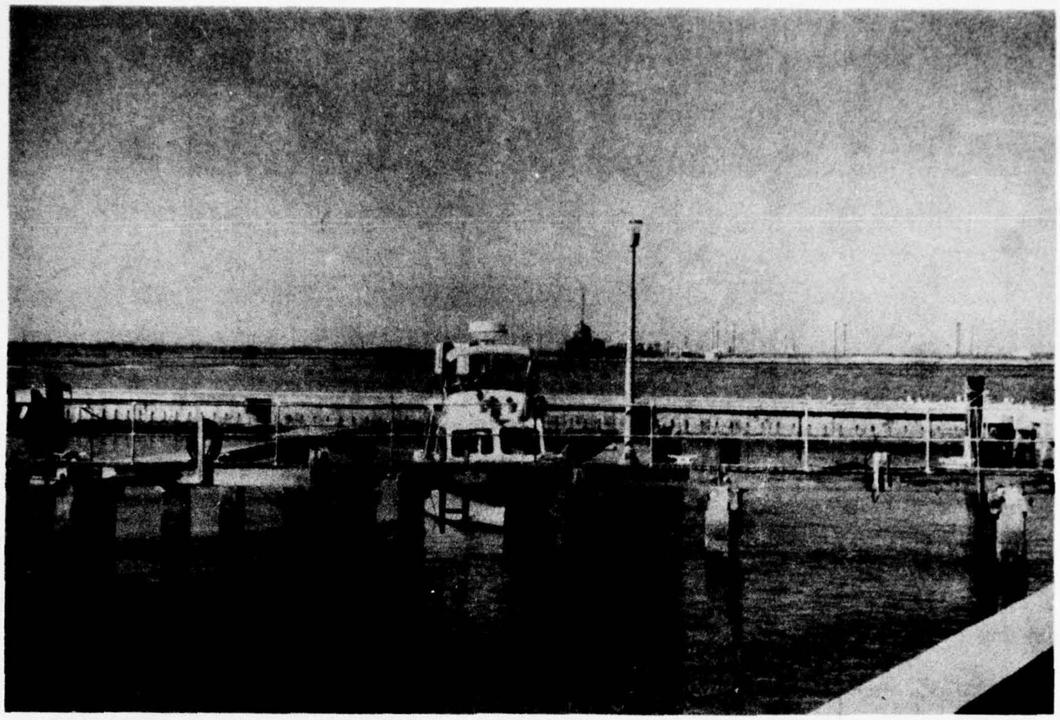


Figure 11. Two Views of Ship Channel and Dock Area Inside of Sea Wall at U.S. Coast Guard Base in Galveston

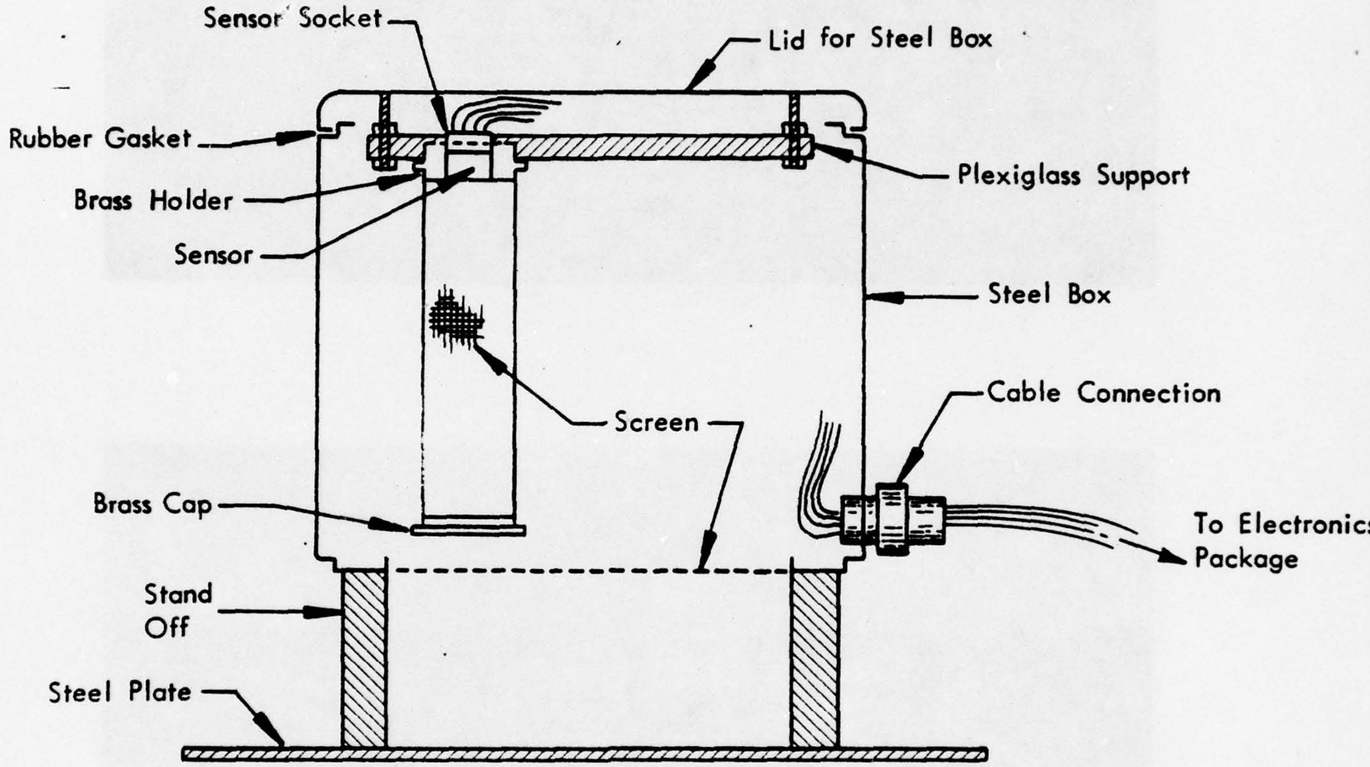


Figure 12. Cross-Section of Sensor Shelter as Designed for Long-Term Monitoring from a Sea Wall (only one of four sensors shown)

Although only one TGS sensor and its enclosure are shown in Figure 12 there were four sensors, all of which possessed the cylindrical brass wind-screen covers and two of which also were covered with sheets of rubber dental dam. Only two sensors were operated at a time and the other two sensors were standby sensors which could be activated by flipping a switch in the sensor enclosure; the presence of the standby sensors was expected to simplify the servicing of the sensor unit from a boat if this should have been required. The standby sensors were not used. In the original design the switch handle extended through the sensor cover; since this broke the water seal to the electronics package, the switch later had to be remounted inside the enclosure to remedy seawater shorting problems.

Figure 13 shows the sensor enclosure with the cover removed; visible in this picture are two Model 812 TGS sensors (screen covers not shown for them). Two other TGS are present but one is covered with a cylindrical wire screen cover (wind-screen) and the other covered with both a screen and a membrane of rubber dental dam (cemented together with a water-based rubber latex). Also shown is this figure is the remote alarm box with its horn, red warning light, alarm reset button and alarm cut-off switch.

3. Electronic Circuitry: The TGS sensor system installed on the sea wall in Galveston consisted of five packages: (1) the sensor enclosure, (2) the electronics package, (3 and 4) the recorder and power supply packages, and (5) the remote alarm package. Figure 14 provides a diagram showing the physical relationships of these individual packages. Two printed circuit boards with the alarm logic and the regulated power supply boards were hermetically sealed inside the electronics package and they are shown in Figures 15 and 16. A six-wire cable (three twisted pairs) greater than 330 ft in length was used to provide DC power to the electronics circuit boards and to the sensors; also, it carried the signals from the two working sensors and the alarm logic circuit to the three strip chart recorders located in a wood box underneath the boat ramp. Another cable from the power supply box carried power to the remote sensor box and also the alarm signal from the electronics package.

Schematics for the TGS oil vapor sensing system including the sensor package, the electronics package and the remote alarm package were presented in Figure 6. The regulated power supplies for the sensors and for this circuitry are shown in schematics given in Figure 7. A block diagram summarizing the functioning of the complete circuit is given in Figure 17.

4. Installation of Buoy System in Galveston: On February 25, Ed Fago and Sandra Dick of Midwest Research Institute met with Lt. Dante Grasso in Galveston at the Coast Guard Base to install the TGS sensor system. The sensor enclosure and electronic package, mounted on a steel plate for support, were placed at the 90 degree bend in the sea wall over 300 ft from the power supplies and recorders (see Figure 18). The metal plate was securely attached to the sea wall by a chain which passed through a hole in the sea wall. This resulted in placement of the sensors between 2-1/2 to 5 ft above the water depending upon the tide.

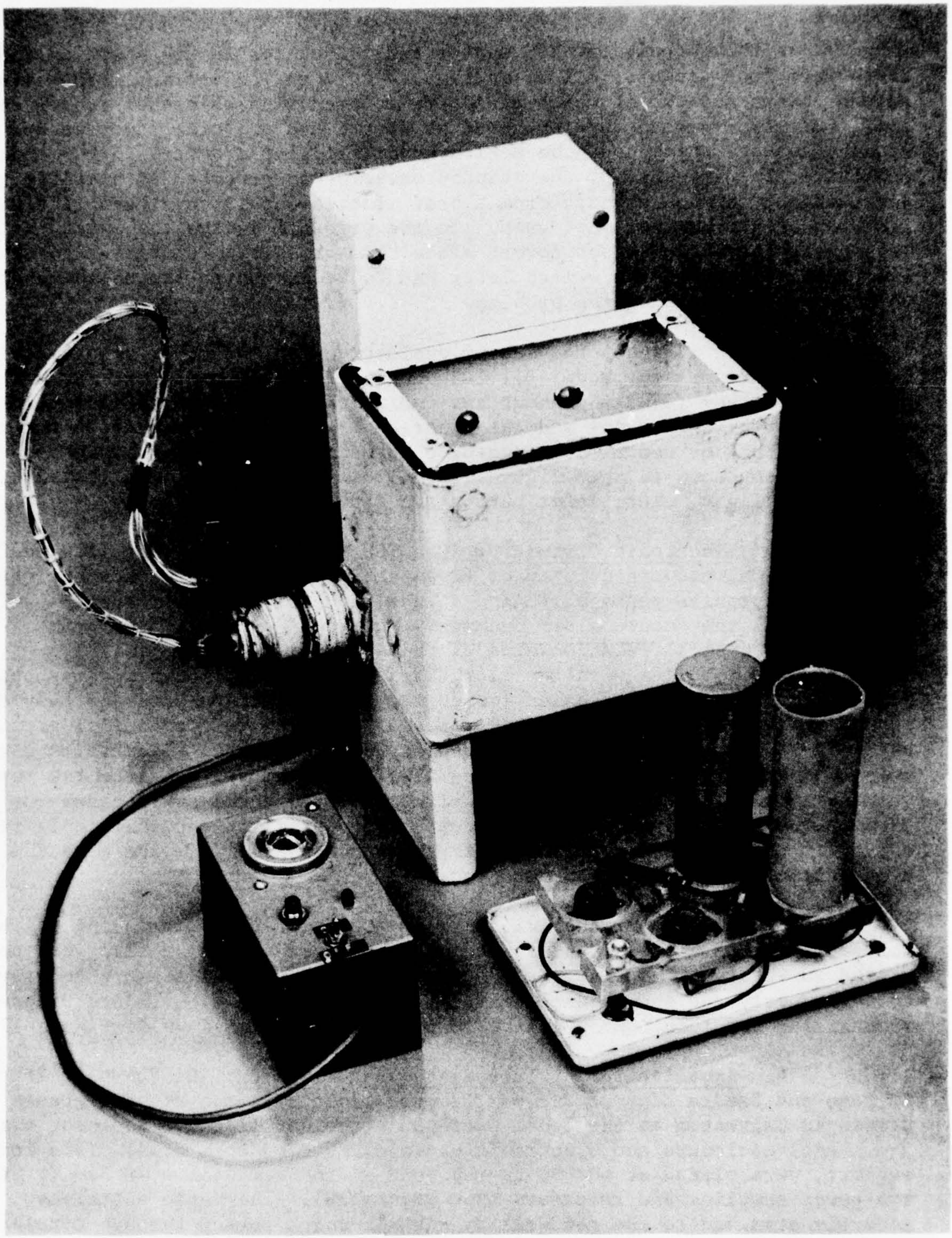


Figure 13. Hydrocarbon Vapor Sensor System with Lid Inverted to Show One Screen-covered Sensor, One Membrane-covered Sensor and Two Uncovered Sensors. Also shown is the Remote Alarm Box.

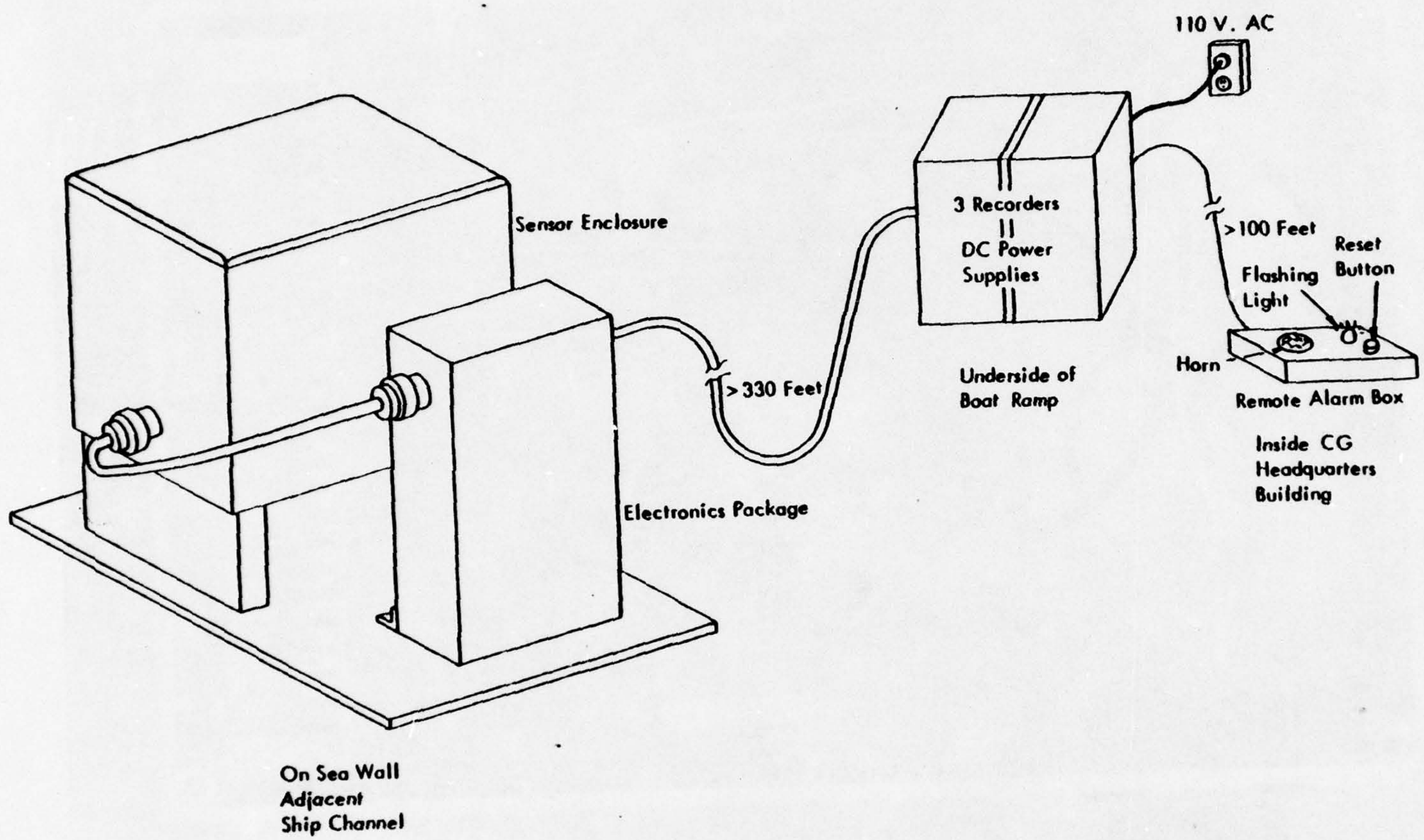


Figure 14. Component Parts and Location at Galveston Installation (not to scale)

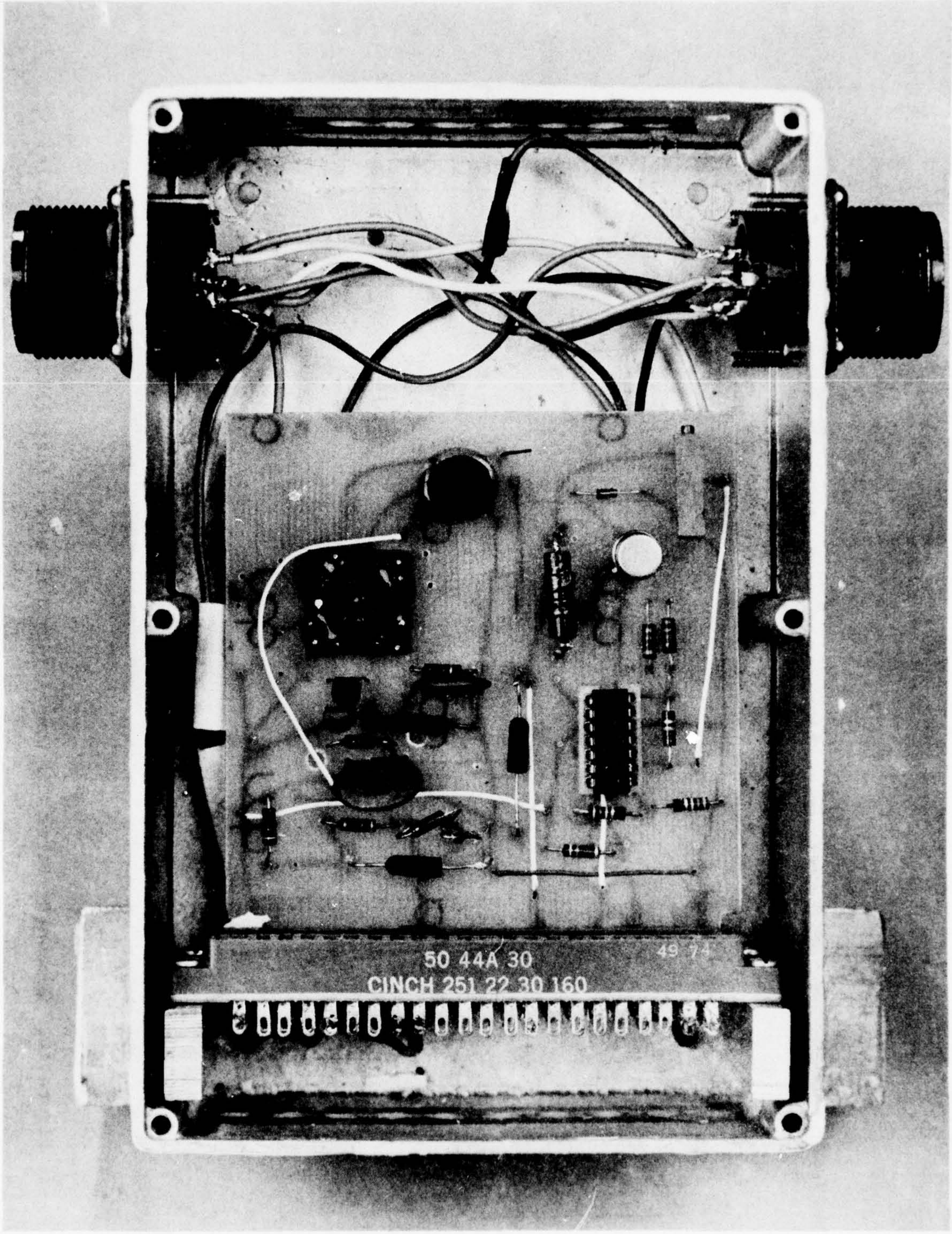


Figure 15. Electronics Package with Cover and Logic Circuit Board Removed. The Regulated Power Supply Board is Shown.

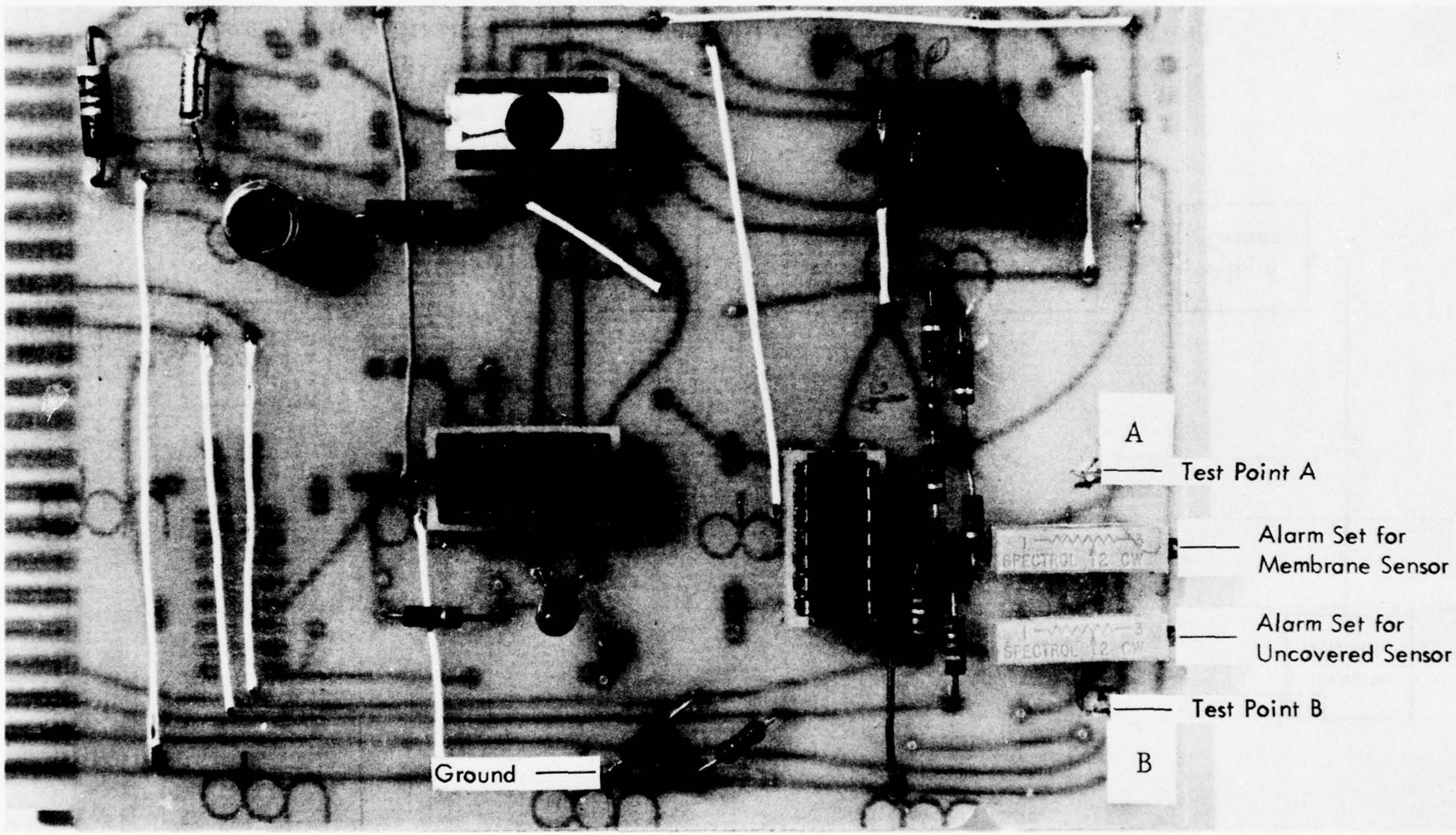


Figure 16. Location of Alarm Threshold Adjustments on Alarm Logic Circuit Board.

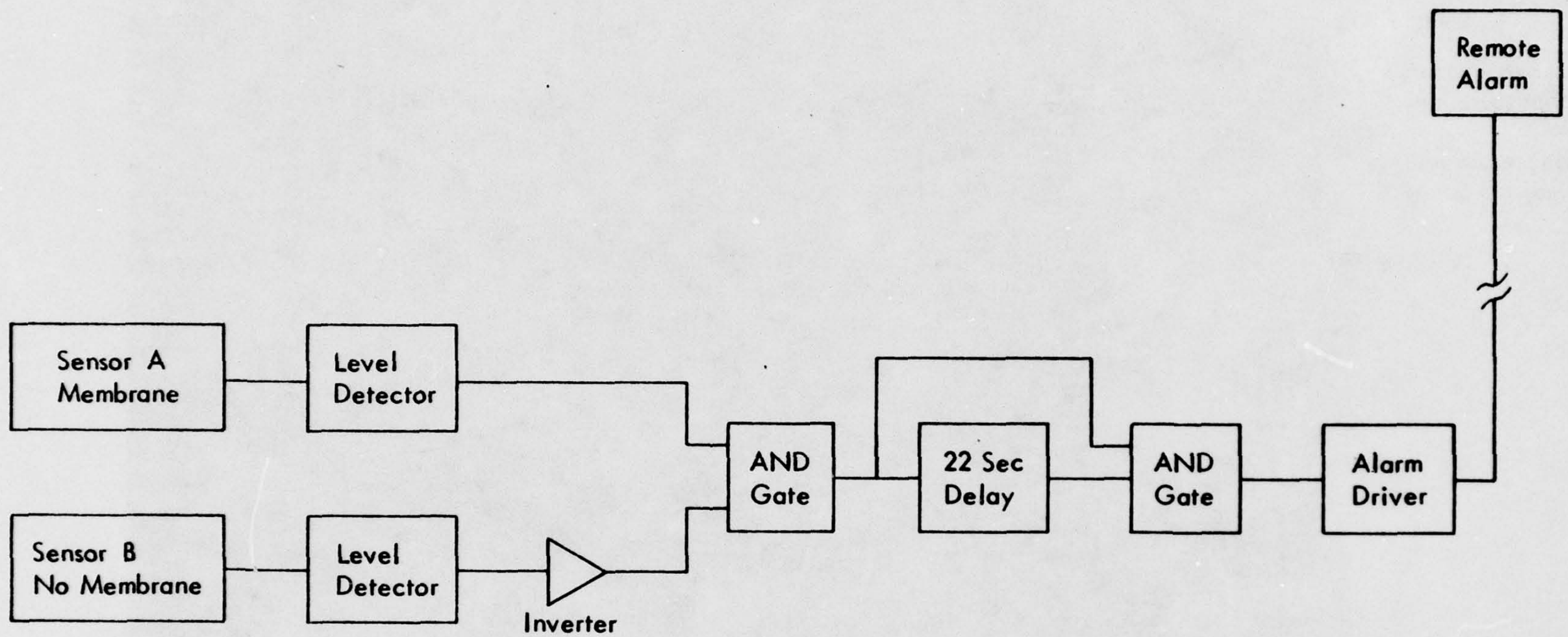
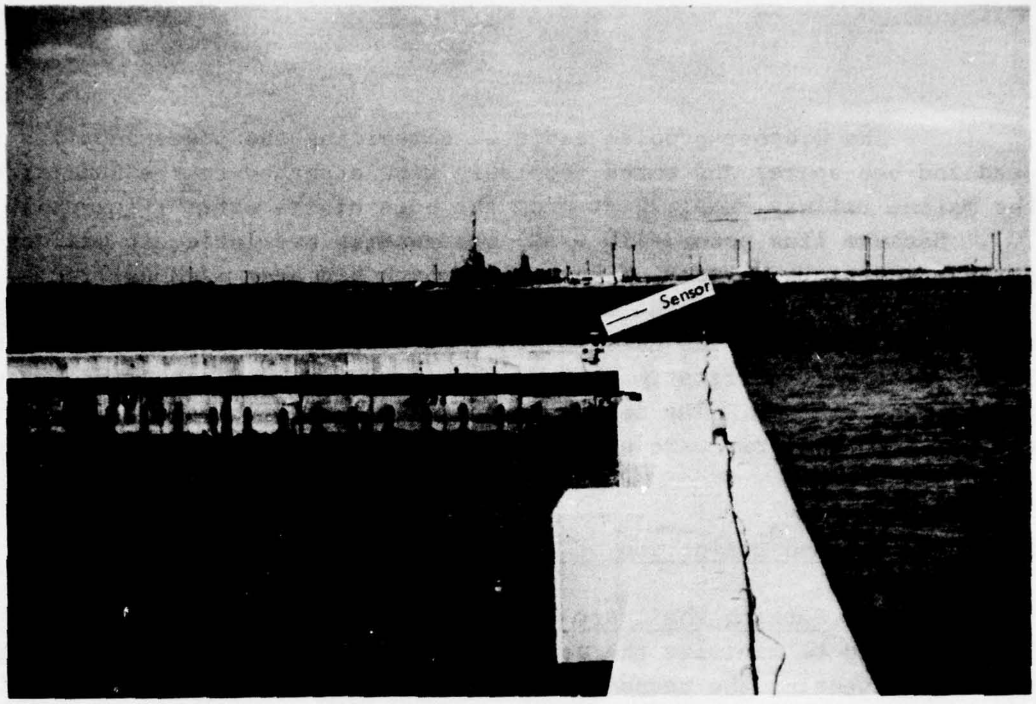


Figure 17. Block Diagram Showing Operation of Electronic Circuits of TGS Oil Vapor Sensing System



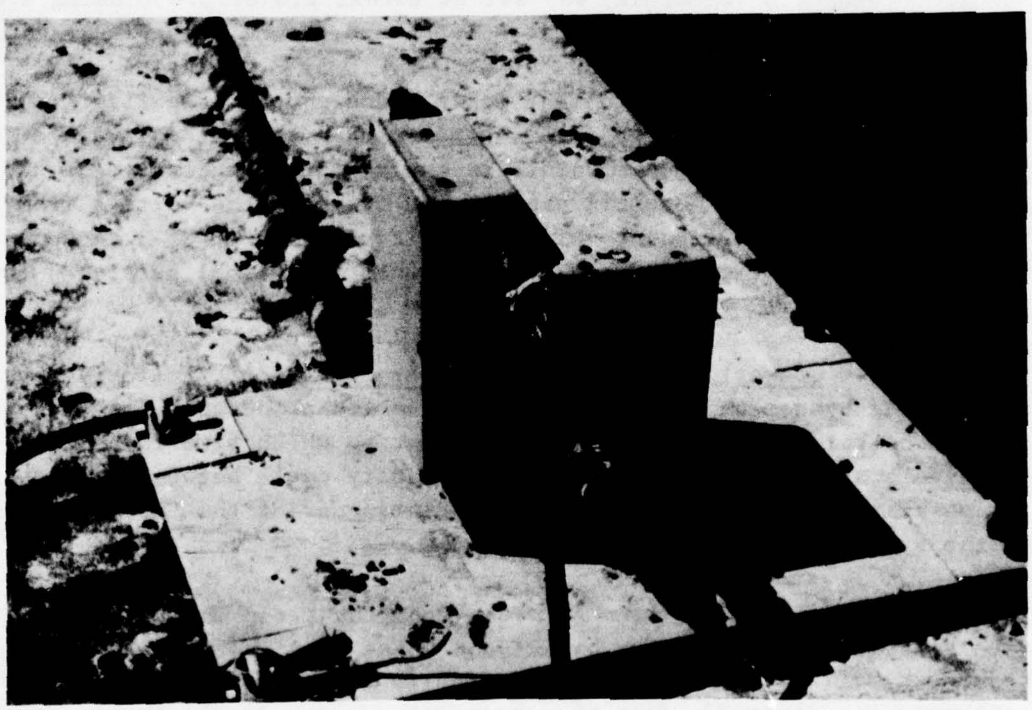


Figure 18. Location of Sensor on Sea Wall (Upper) and Close-Up of Hydrocarbon Vapor Sensor Installed on Sea Wall

The weather-proofed cabinets containing the power supplies (one used and one spare) and three recorders were attached to the underside of the marine railway ramp, 20 ft from the edge of the water (Figures 19 and 20). Because line power (110 V AC) was readily available, it was used to power the sensors instead of batteries which had been used earlier. The remote alarm box consisting of a Sonalert , a flashing light and a reset button was placed in the Coast Guard control room. A log for recording the time of alarms, verification and weather was kept by Coast Guard personnel in the control room. The sensor response tracings, the alarm logic tracing and the log of alarms were used to evaluate the performance of the system.

H. Operation and Evaluation of Prototype Oil Detection System

1. Setting the Alarm Thresholds: In the present system an alarm logic is used to minimize the sensitivity of the system to exhaust vapors without preventing the response of the system to oil fumes. During the preliminary studies the alarm thresholds were set arbitrarily at different levels in an effort to obtain maximum selectivity with least loss in sensitivity and no false alarms. The following alarm thresholds have proven satisfactory:

Sensor A (membrane) was set at either 2.0 or 3.0 V using a high impedance volt meter connected to Test Point A and ground (see Figure 14). In the same manner Sensor B was set at either 2.0 or 3.0 V using a high impedance volt meter connected to Test Point B and ground (see Figure 14). With these settings high voltages (i.e., greater than the set points) for both sensors will signal no alarm. This is the condition encountered when engine exhaust was sampled. When oil vapors were present, the voltage from Sensor A remained below the set point while the voltage from Sensor B exceeded the set point. This condition produced an alarm when the signal persisted for as long as 22 sec.

2. Operation of Sensor System at Galveston: Following installation of the system on the sea wall in Galveston as described above, the sensor was operated for a number of months during which time there were some failures most of which were traced to a faulty cable between the sensors and the power supplies. Typical data accumulated during the "normal" operation of the system in Galveston is described.

Much data have been gathered from the strip chart recorders which were serviced every few days by MRI and Coast Guard personnel. The charts have been mailed to MRI for study. Figures 21 and 22 reproduce the data collected May 24 to 27, from the three recorders. In the top of each figure is given the alarm logic tracing; the center curve is from the covered sensor and the lower curve is from the uncovered sensor.

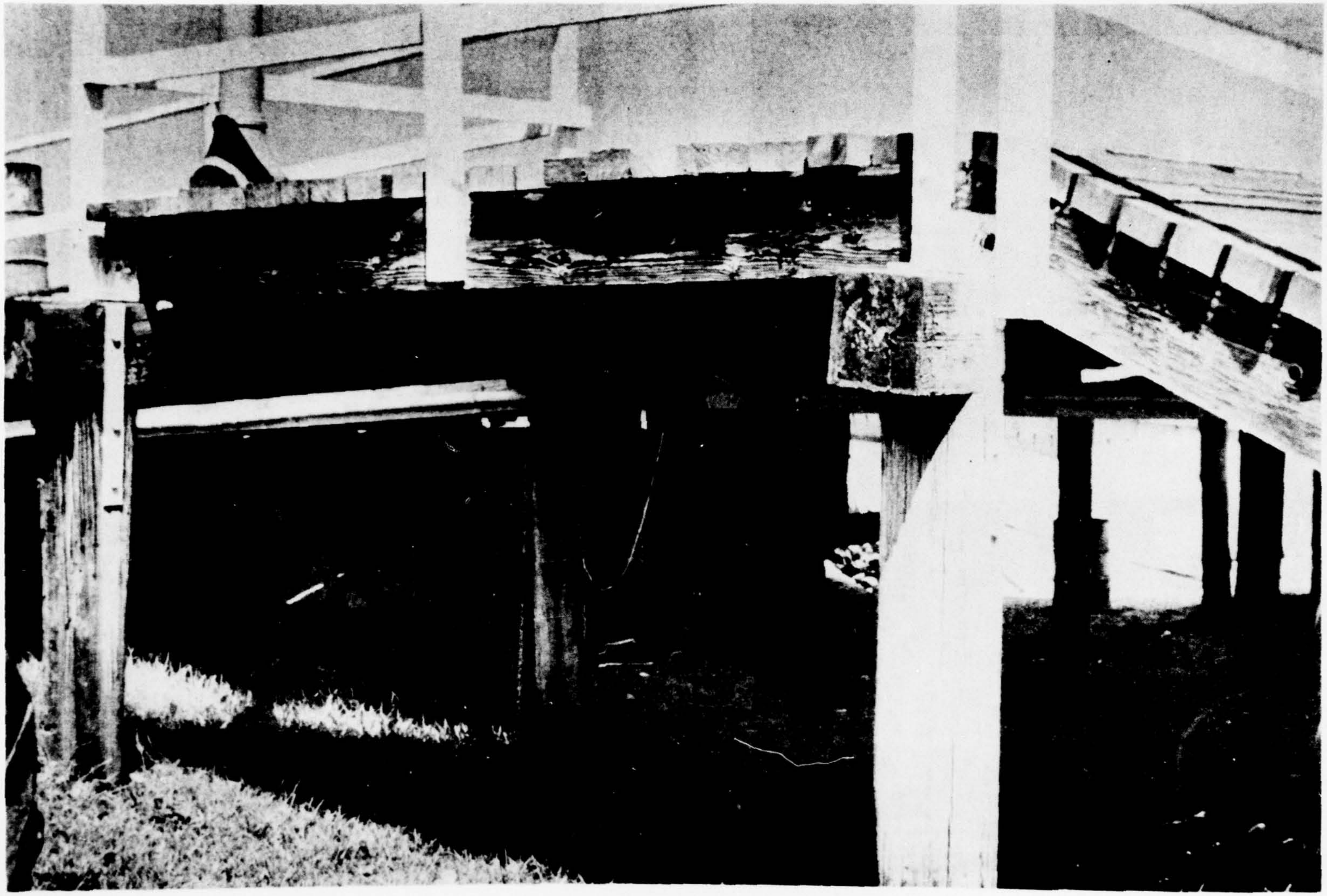


Figure 19. Marine Railway Ramp with Power Supplies and Recorders Hung from Its Underside

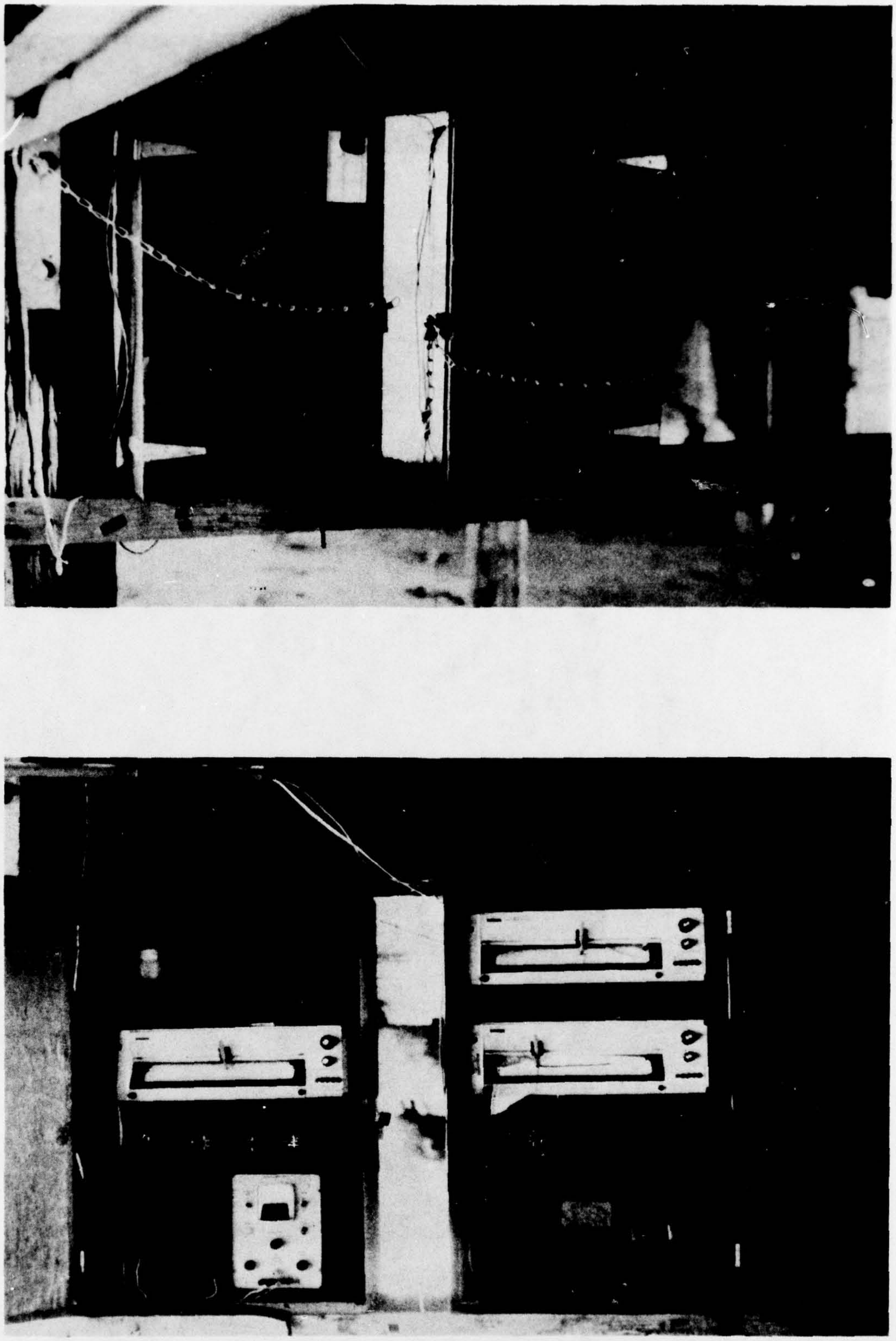


Figure 20. Enclosures, Recorders and Power Supplies Located Under Boat Ramp

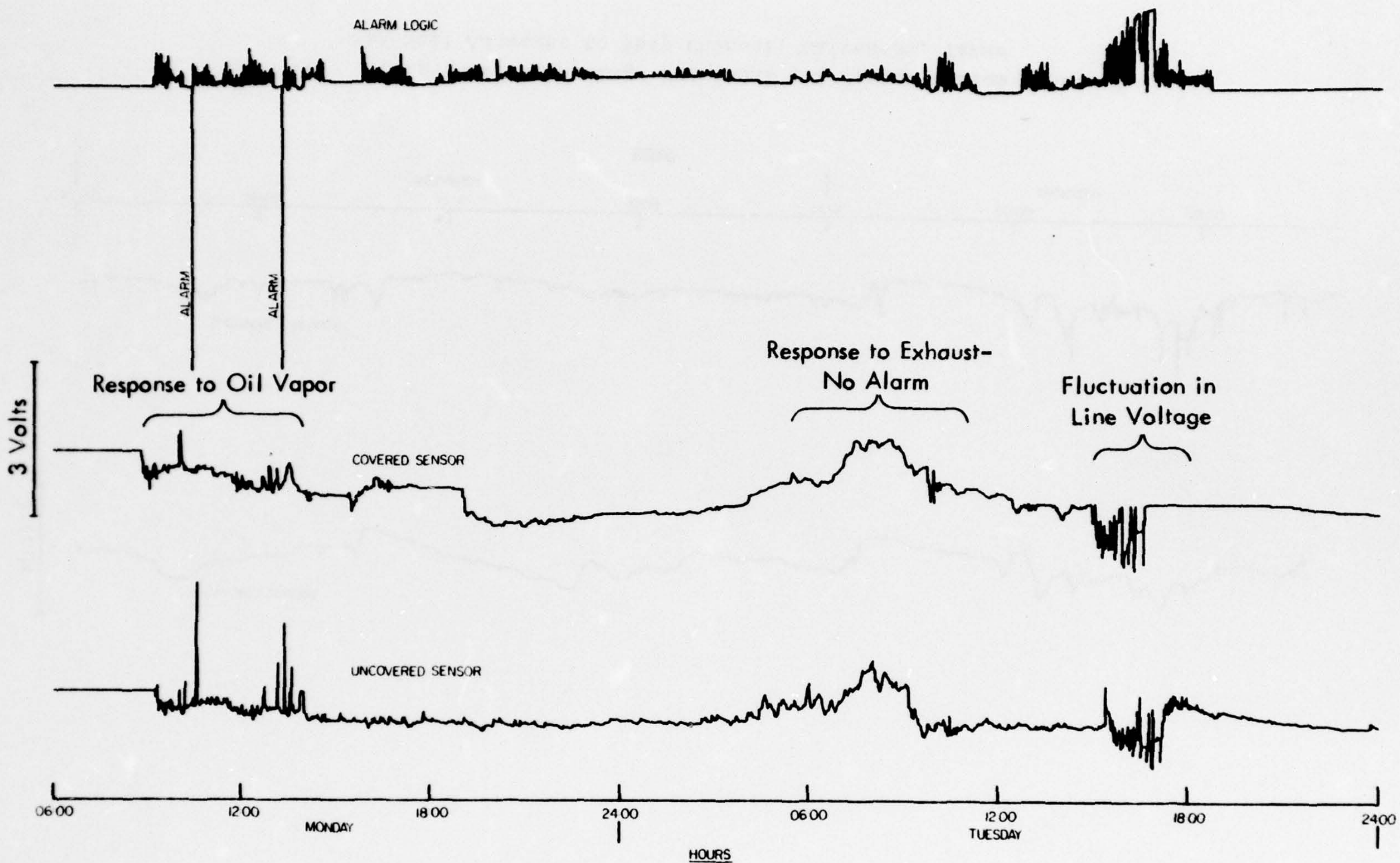


Figure 21. Strip Chart Recordings From Dual TGS Sensor System Operated On Sea Wall Adjacent To Ship Channel, Galveston, Texas

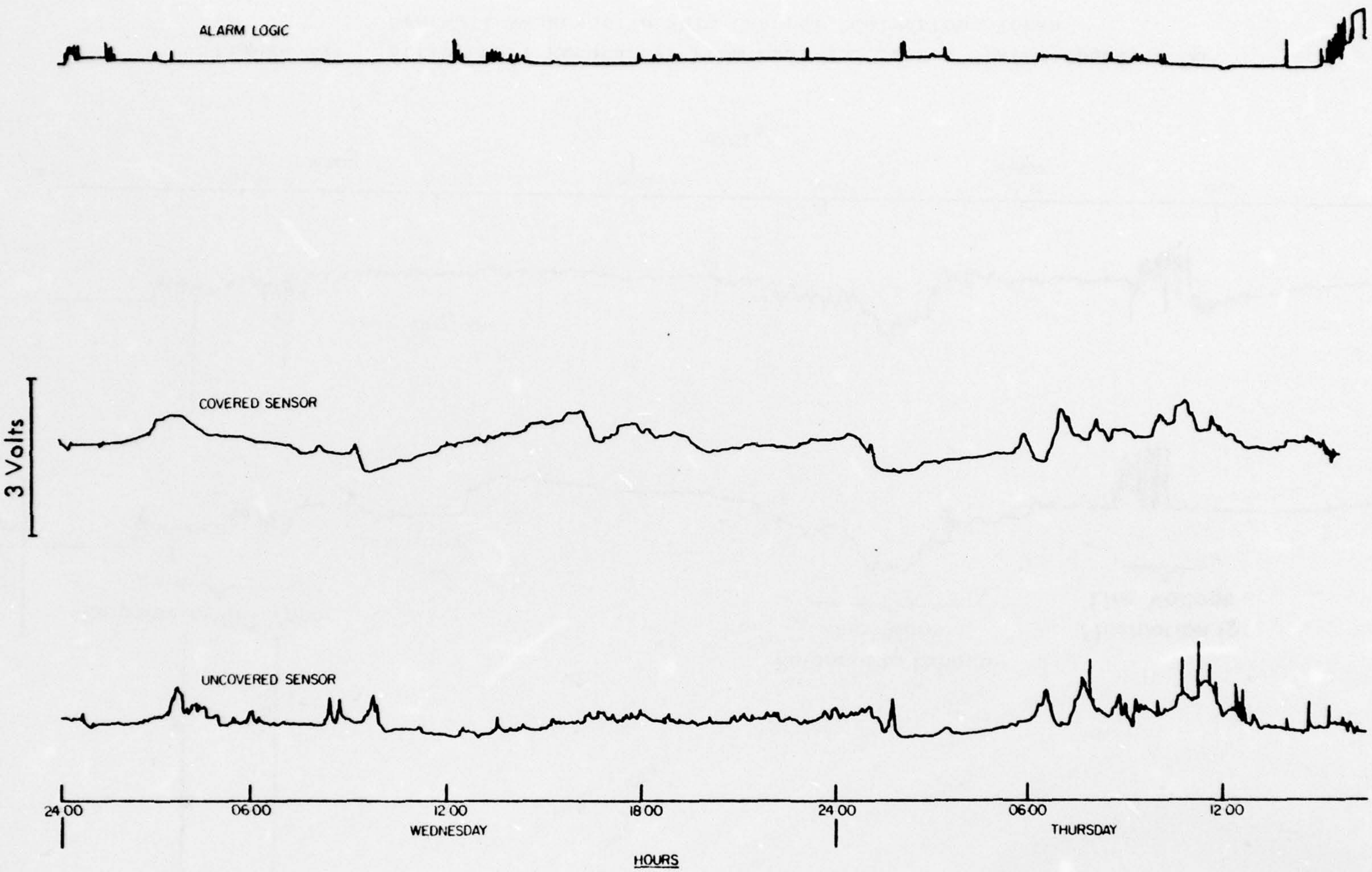


Figure 22. Strip Chart Recordings From Dual TGS Sensor System Operated On Sea Wall Adjacent to Ship Channel, Galveston, Texas

At about 10:00 and 13:00 hr Monday, alarms were signalled; comparison of signals from the uncovered and the covered sensors shows that the response was much greater for the uncovered sensor--a circumstance which has been programmed to give alarms. At around 0800 hr on Tuesday both sensors responded well to the vapors and no alarms were signalled; it is concluded that this response was to exhaust from one of the Coast Guard's boats and that no alarm should have been signalled.

At 1600 hr on Tuesday there was much noise in all three tracings; it is suspected that there was a problem with the 110 V AC power lines to the power supplies feeding the system since the same type of response has been obtained with the duplicate system in the laboratory by manually varying the voltage supplied to the circuitry. Consideration is being given to the possible use of a voltage regulatory circuit to prevent this type of noise.

Examination of the tracings for Wednesday and Thursday show some responses of both covered and uncovered sensors but apparently the magnitude of the responses was too low to trigger the alarm. It looks as though some oil may have been on the water on Thursday morning but there was no alarm because the alarm threshold was set too low or perhaps because of a windy condition which diluted the vapors significantly before they reached the sensors. Unfortunately we have received no data on either the atmospheric conditions or the presence of oil during this test period.

There were some spurious signals in the control room from the TGS sensors. These appear to have been caused by an occasional intermittent short in the cable to the control room. However, these were not shown by the three tracings. Most of the time the tracings mailed to us by the Coast Guard showed that the sensors and alarm logic were working correctly and that the remote signals agreed with the logic tracing.

In an effort to correlate some of the signals obtained with operation of Coast Guard craft in and out of the base in Galveston, a log showing the operation, light-off, and other activities of one of the 210 ft medium endurance cutters was supplied to us. No direct correlation between the operation of the 210s and the signals from the uncovered sensors was possible. Obviously there were ships of all descriptions passing by the sensor in its position on the sea wall and these appear to be responsible for the "exhaust" responses seen.

Most of the charts generated at Galveston look like the chart reproduced in Figure 21 except that the noise in the alarm logic tracing was absent. A cyclic change in baseline voltage of the membrane-covered sensor is evident in Figure 21. Apparently in the early morning hours there is a gradual increase in baseline voltage which continues until about 10:00 PM, after which it falls to its original value. It is judged that this curve corresponds roughly to the major daylight hours and also to the major boat and ship traffic. The meaning of this baseline voltage change is unclear,

but possibly could be due to the absorption and desorption of rubber soluble pollutants--primarily hydrocarbon vapors. Fortunately this does not trip the alarm nor does it interfere with an alarm when oil is present.

Figure 23 presents some additional sensor performance data while the system was located on the sea wall at Galveston; in this tracing the amplitude of the signals was tripled to show the response of boat traffic and/or air pollutants in the area. At 0817 hr the USCG Valiant returned to its dock inside of the enclosure by the sea wall. Although there was exhaust noise at this time the exhaust signals were weak and could not be distinguished from the other noise. No alarms were signalled during the period shown in this figure.

Again, the gradual increase in baseline voltage for the membrane sensor from 0600 hr to 1130 hr is shown and this tracing shows why the threshold voltage on membrane sensor should be set at 2 or 3 V in order to avoid false alarms and to keep the system functioning properly.

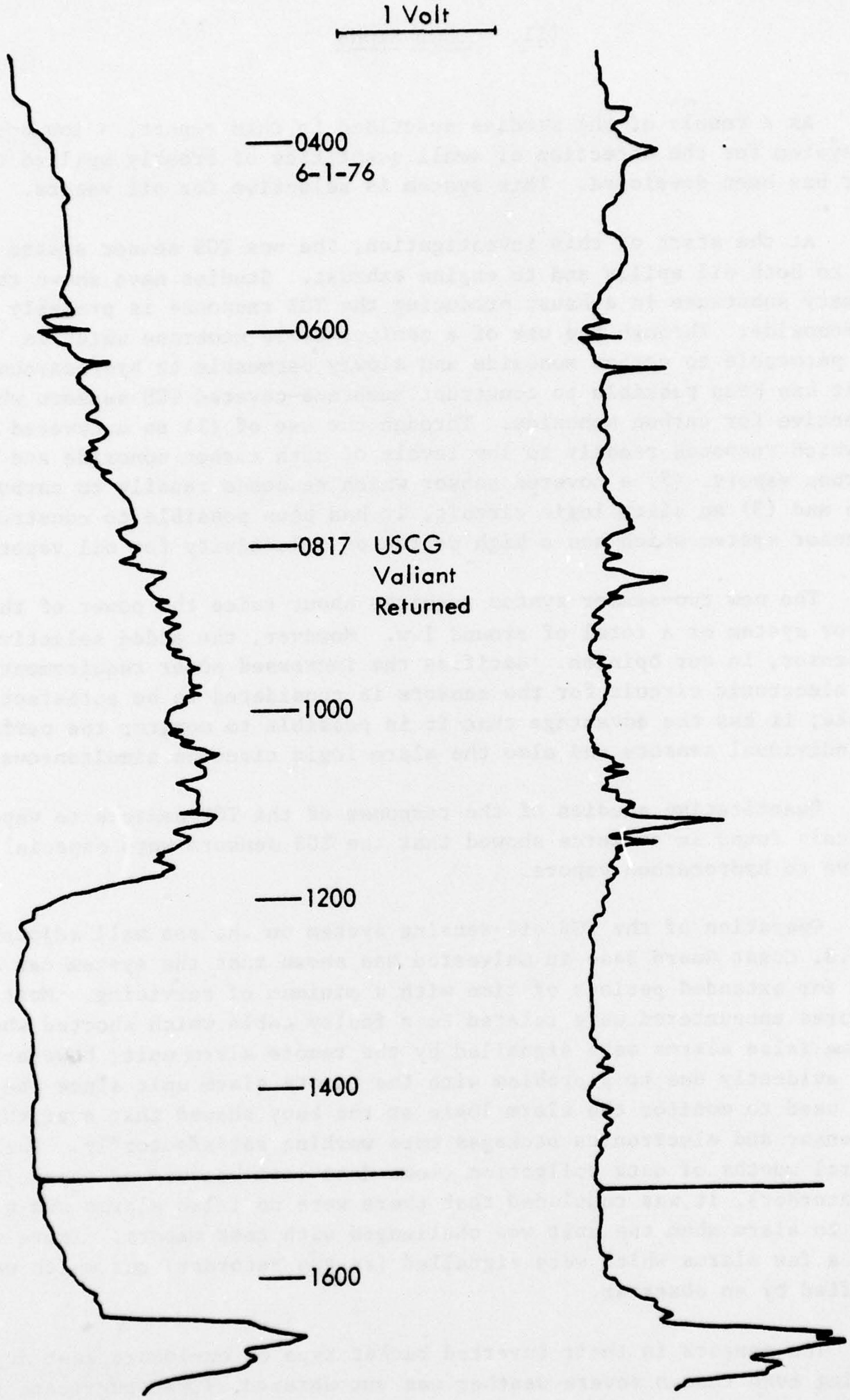


Figure 23. Upper Curve Shows Response of Screen Covered to Exhaust from Boats and Ships in the Ship Channel at Galveston, Texas. Lower curve was made simultaneously with a membrane covered sensor. No oil spills were present or signalled in this period.

III. CONCLUSIONS

As a result of the studies described in this report, a low cost sensor system for the detection of small quantities of freshly spilled oil on water has been developed. This system is selective for oil vapors.

At the start of this investigation, the one TGS sensor system responded to both oil spills and to engine exhaust. Studies have shown that the primary substance in exhaust producing the TGS response is probably carbon monoxide. Through the use of a semipermeable membrane which is rapidly permeable to carbon monoxide and slowly permeable to hydrocarbon vapor, it has been possible to construct membrane-covered TGS sensors which are selective for carbon monoxide. Through the use of (1) an uncovered TGS sensor which responds readily to low levels of both carbon monoxide and hydrocarbon vapors, (2) a covered sensor which responds readily to carbon monoxide and (3) an alarm logic circuit, it has been possible to construct a two-sensor system which has a high degree of selectivity for oil vapors.

The new two-sensor system requires about twice the power of the one-sensor system or a total of around 1 w. However, the added selectivity of the sensor, in our opinion, justifies the increased power requirement. The new electronic circuit for the sensors is considered to be satisfactory and stable; it has the advantage that it is possible to monitor the performance of the individual sensors and also the alarm logic circuits simultaneously.

Quantitative studies of the response of the TGS sensors to vapors of chemicals found in commerce showed that the TGS sensors were especially responsive to hydrocarbon vapors.

Operation of the TGS oil-sensing system on the sea wall adjacent to the U.S. Coast Guard Base in Galveston has shown that the system can function for extended periods of time with a minimum of servicing. Most of the failures encountered were related to a faulty cable which shorted when wet. Some false alarms were signalled by the remote alarm unit; however, this was evidently due to a problem with the remote alarm unit since the recorder used to monitor the alarm logic at the buoy showed that everything in the sensor and electronics packages were working satisfactorily. During the several months of data collection (some data lost because of paper jam on the recorder), it was concluded that there were no false alarms and no failures to alarm when the unit was challenged with test vapors. There were however, a few alarms which were signalled (at the recorder) but which were not verified by an observer.

The sensors in their inverted bucket type of enclosure kept dry and working even though severe weather was encountered. Even hurricane type of weather with waves covering the enclosure did not interfere with its operation.

IV. RECOMMENDATIONS

It is recommended that the two-sensor system using TGS sensors be subjected to further test and evaluation to determine its performance under a wider variety of pollutant vapors and/or atmospheric conditions. Also, there is a need to establish the servicing requirements necessary to keep the system in operation. A problem with the most recent study was the inability of the Coast Guard Personnel to watch the ship channel to verify the presence or absence of spills at the time that alarms were signalled. It is primarily for this reason that additional studies are needed to correlate performance with presence of fresh spills.

Failure of the rubber dental dam membranes used to cover the sensors occurred at about 90 days. To make sure that the system is functioning properly during additional testing, it is suggested that the rubber dental dam be inspected monthly and changed every 90 days. It is also suggested that the reference voltage settings be checked at monthly intervals although there is no evidence to indicate that they might change with time.

Studies should be conducted to determine a means for reducing the power consumption of the TGS sensor system. One possible means of doing this is to operate the sensors on a "duty cycle" which will leave the current turned off more than half of the time. If the sensors are to be line operated, there is no need to use the duty cycle. Another possibility is the substitution of the Figaro Gas Sensor No. 711 for the No. 812 sensor used under the rubber dental dam membrane. The 711 sensor has a high sensitivity to CO and a power requirement of 250 mw at 5 v according to the published specifications for this sensor.

APPENDIX

FIGARO GAS SENSOR NO. 812

General Purpose Transducer

FIGARO GAS SENSOR #812

1. Distinctive Features

In comparison with conventional TGS sensors,

a. Designed for 5.0V heater operation instead of 1.0V, 1.2V or 1.5V as previously required.

b. Has improved long term stability.

2. Configuration

As shown in Fig. 3. Current #812 sensors are as shown in sketch (a), but future production will adopt the layout shown in sketch (b).

3. Electrical Specifications

- Heater Volts .... 5.0 ± 0.2V
- Heater Power Consumption 620mW
- R (IB 1000) .... 1kΩ ~ 10kΩ
  This represents sensor resistance when exposed to 1000-ppm Isobutane in air.
- R (IB 3000)/R (IB 1000) ...... approx. 0.55
  This represents ratio of
  sensor resistance in 3000-ppm Isobutane/
  sensor resistance in 1000-ppm Isobutane.
- Sensitivity Characteristics
  to various gases .... as shown in Fig. 9.
- Warm-up Time .... within 2 minutes.
- Dependency on Temperature
  and Humidity .... Same as for conventional sensors.

4. Recommended Testing Procedures

a. The sensor operates with either D.C. or A.C.

b. Set heater volts at 5.0V ± 0.2V using a stabilized supply.

c. To establish the sensor's characteristics its resistance may be measured as shown in Fig. 4.

d. When a digital multimeter is employed for resistance measurement, in general, the resistor under test is connected to the meter's built-in constant current source. The voltage developed across the resistor by this current is measured by the meter and displayed as resistance.

When the sensor resistance (R) is measured on the digital multimeter with the constant current (I_S), Joule heat ($I_S^2 \cdot R$) will be generated in the sensor. Maximum heat will occur when the sensor has reached its highest resistance state in fresh air. Less heat will be produced as the sensor resistance falls due to the presence of deoxidizing gas.

An excess of the current produces undesirable amount of heat in the sensor resulting in a deterioration of its long term stability. To avoid damage to the sensor's long term stability please ensure that not more than 0.5mA can be supplied by the multimeter employed.

e. Figures 10, 11, 12 and 13 show practical examples of gas-leak detector circuit. Figures 14 and 15 show output voltage V_M and $V_{2k\Omega}$ in relation to gas concentration obtained from the circuits in Figs. 11 and 13 respectively. In addition gas response curves obtained from these circuits are shown in Figs. 16 and 17 respectively.

In the circuits in Figs. 10 and 12 the ratio of the output-voltage change to gas-concentration change is relatively small resulting in poor repeatability in terms of alarm setting when compared with that produced by the cirucits in Figs. 11 and 13. The former circuits are practically convenient because of their simple construction. However, the circuit in Fig. 11 is recommended when the best repeatability in terms of alarm setting are required.

f. The circuits shown in Figs. 10 and 11 are designed to produce an output proportional to the conductance of the sensor. The constants applicable to these circuits are determined by consideration of the sensor's characteristics, in particular the value of current flowing through the sensor. In these circuits nearly 0.03mA of current flows through the sensor when placed in fresh air. The current increases as the concentration of gas increases, but it does not increase more than approximately 1mA being limited by circuit volts (V_C) and Adjustable Resistor (R_{ADJ}). When a circuit is designed in accordance with the component values given in Figs. 10 and 11 no deterioration of long term stability of the sensor due to the undesirable amount of Joule heat will occur.

g. Figures 12 and 13 include a series resistor connected with the sensor. The voltage across this resistor is used to trigger a thyristor. In both cases the circuit current in fresh air is less than 1mA and reaches maximum values of 1.25mA and 5.0mA respectively in gas.

No thermal damage of the sensor caused by the Joule heat will occur when the recommended component values are maintained. If any circuit changes are considered necessary e.g. changing the value of the series resistor or increasing V_C to a maximum of 30 volts, then the new heating effect produced in the sensor must be checked with a view to ensuring that the heat input does not exceed that experienced when using the recommended circuits.

h. Table 2 is to show the recommended component values to be used in Figs. 10, 11, 12 and 13.

TABLE 2. RECOMMENDED COMPONENT VALUES FOR FIGS. 10, 11, 12 & 13

Figures	10	11	12	13
Heater volts V_H(V)	5±0.2	5±0.2	5±0.2	5±0.2
Circuit volts V_C(V)	5	10~15	5	10
Series resistor R_L(kΩ)	–	–	4	2
Adjustable resistance value R_{ADJ}(kΩ)	50	100	–	–

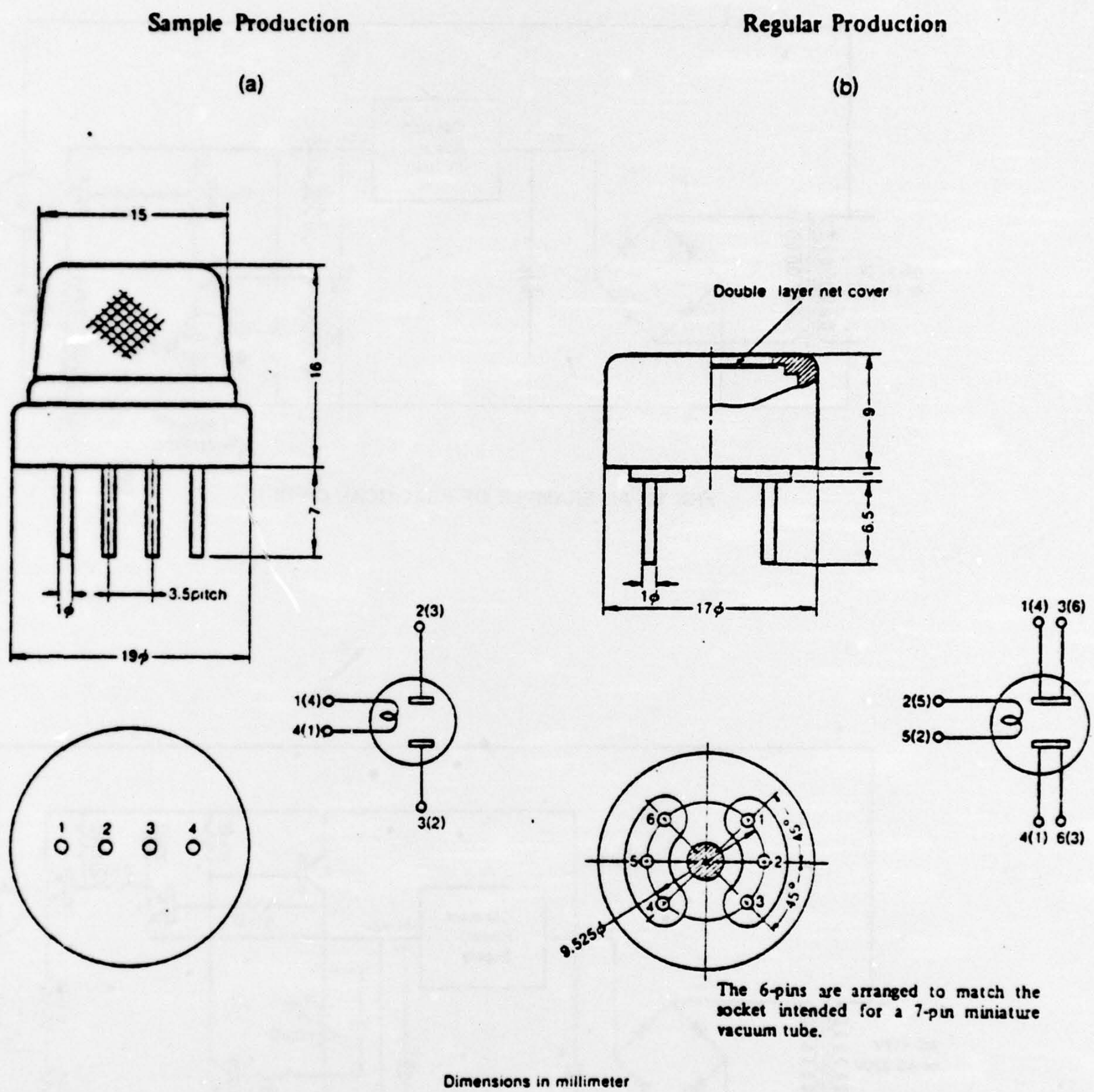


FIG. 3. CONFIGURATION OF # 711 & # 812.

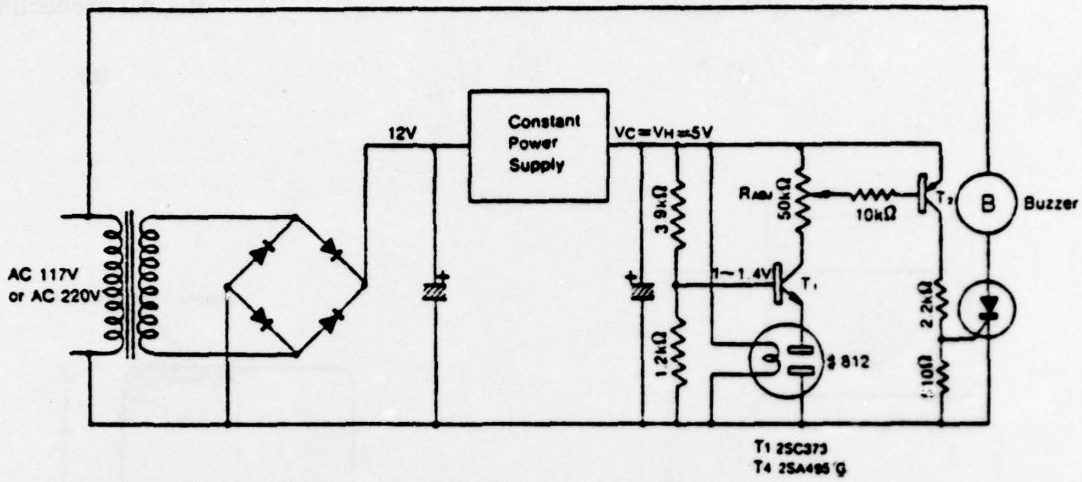


FIG. 10. AN EXAMPLE OF PRACTICAL CIRCUIT.

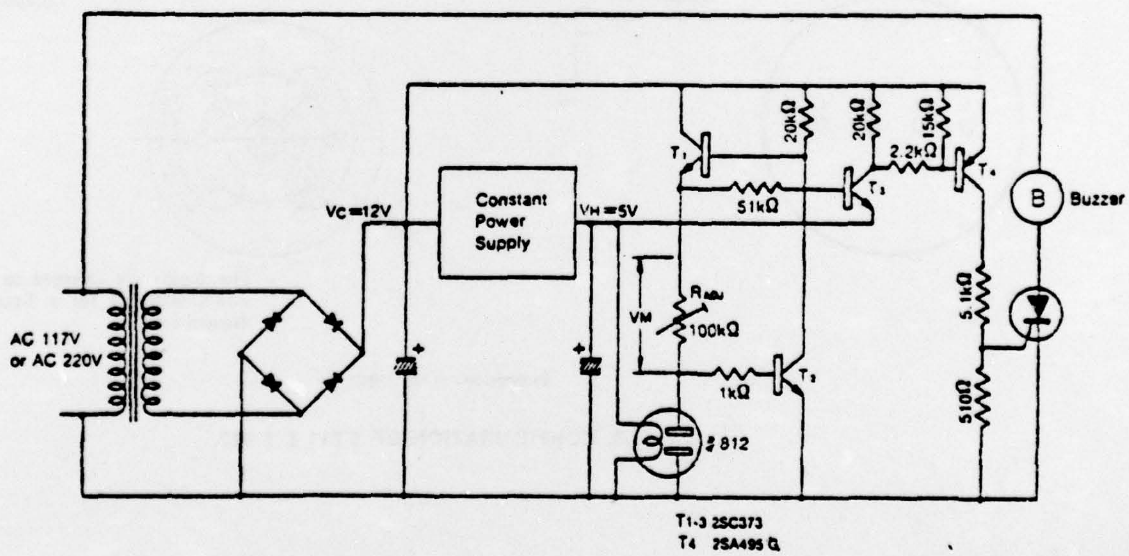


FIG. 11. AN EXAMPLE OF PRACTICAL CIRCUIT.

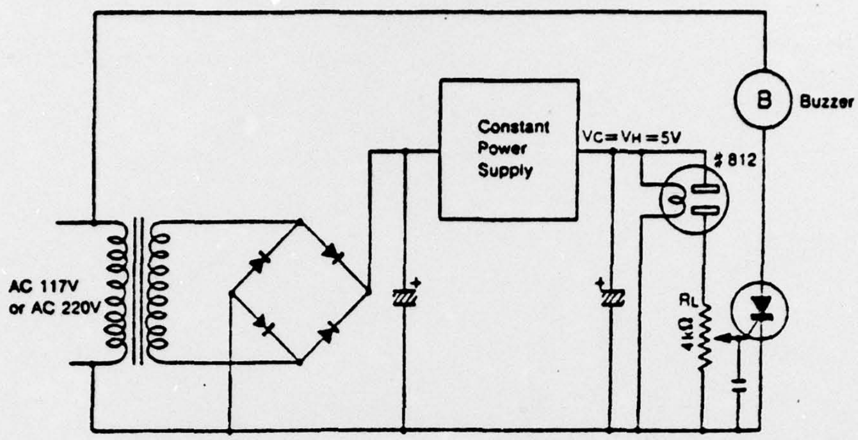


FIG. 12. AN EXAMPLE OF PRACTICAL CIRCUIT.

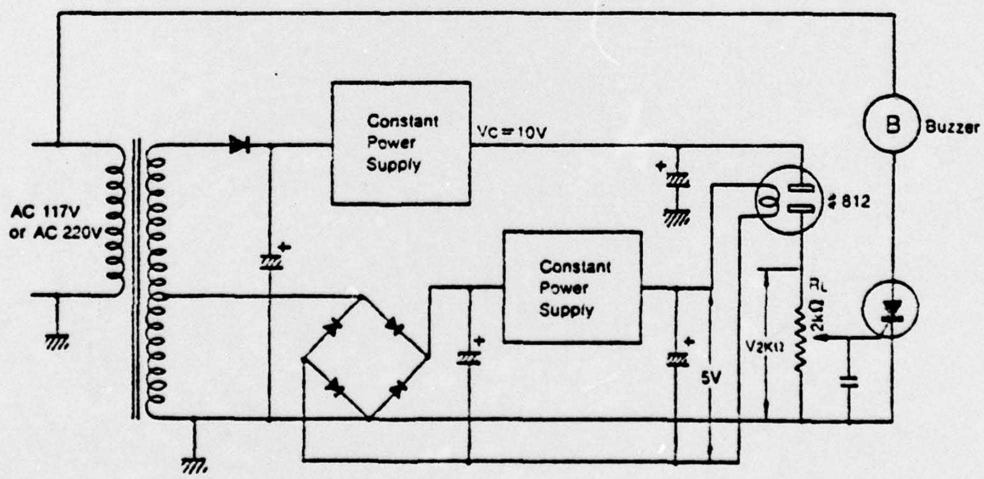


FIG. 13. AN EXAMPLE OF PRACTICAL CIRCUIT.